Journal of Chromatography, 640 (1993) 167–178
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2733

Comparison of silica-based and polymer-based cation exchangers for the ion chromatographic separation of transition metals

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ABSTRACT

Silica gel- and polymer-based exchangers differ not only in the substrate but usually also in the structure of their sulphonic acid exchange group. The performance and chromatographic behaviour of modern macroporous poly(styrene–divinylbenzene) polymers of 5-μm particle size after surface sulphonation were examined. Further, two commercially available silica gel cation exchangers were investigated as references for what is now possible and how the chromatographic performance is influenced by the substrate and the structure of the exchange site. The influence of the capacity of surface-sulphonated exchangers for acid and complexing eluents, which are necessary when transition metals are to be separated, was studied. The interaction of polarizable metal cations with the π-system of the polymer depends on the resin capacity, and a comparable dependence for H^+ and complexing eluents was found. The distance of the functional group from the core influences the adsorption effects dramatically. Lowering the non-specific interaction increases the chromatographic efficiency rapidly. The performance of silica gel-based exchangers is nearly one order of magnitude better than that of surface-sulphonated exchangers. The selectivity of the exchangers investigated is strongly dependent on the structure of the exchange site and on the resin capacity.

INTRODUCTION

The application of cation chromatography (CIC) is routinely limited to the determination of alkali and alkaline earth metal ions in drinking water or high-purity water for microelectronic purposes [1–4]. The analysis of heavy and transition metals is normally done by atomic spectrometry, but CIC offers some unique advantages, namely non-destructive separation [1], speciation analysis [1,5–7], low absolute detection limits and low costs [8]. A specific advantage in comparison with atomic spectrometry is the ability to determine molecular ions such as ammonium compounds or alkyl–metal cations [1–4,9].

The combination of trace-matrix separation (TMS) via cation exchange and the preconcentration capabilities of ion exchangers allows ultratrace analyses in complex matrices such as refractory metals using CIC [8].

Modern powerfull HPLC cation exchangers are based on silica gel. The advantage of silica gel over polymers is their narrow particle size distribution, which is about half that for polymers. The functionalization is strictly held on the surface, which dominates for the observed rapid mass transfer [10,11].

A disadvantage for the routinely use of silica-based cation exchangers is the solubility of silica gel in all aqueous solvents, which leads to a continuous decrease in exchange capacity and also a decrease in chromatographic performance. This effect must be continuously compensated for by adjusting the elution system. Every elution system described in the literature in strongly dependent on the lifetime of the column used and therefore exactly reproducible only with substantial expertise. Drawbacks of silica gels for combined TMS and CIC separation is the

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limited pH range of 2–7 and the incompatibility with fluoride-containing samples. These points are extremely important if trace separation and preconcentration are necessary [8].

The advantage of porous poly(styrene–divinylbenzene) (PS–DVB) packings is their high chemical stability. Nevertheless, PS–DVB materials show often a slow mass transfer through the chromatographic bead that leads to poor chromatographic efficiency [11]. An attempt to overcome this shortcoming was made by chemical modification of commercially available PS–DVB resins of 5 μm diameter, a narrow size distribution and extremely high cross-linking. The pore size of these resins is comparable to that of the most powerful cation exchangers based on silica gel. The resins were sulphonated with concentrated sulphuric acid and silver sulphate as catalyst. The exchange capacity, Q_g, of the resins was determined under different sulphonation conditions (reaction time and temperature) and varied in the range $Q(H^+) = 0.3$–1.9 mmol/g.

A popular elution system for the analysis of the most common di- and trivalent ions is the tartaric acid–base system, where the base can be an alkali metal hydroxide or ammonium derivatives [8]. The analytical power of this elution system in combination with the chromatographic efficiency of the HPLC cation exchanger Nucleosil 5SA permits the simultaneous analysis of up to twelve ions in a single isocratic run (Fig. 1).

The most common silica based HPLC-exchangers, Nucleosil SA, RoSil CAT (now BioSil CAT) and a dynamically coated cation exchanger based on RoGel, were compared with laboratory-modified polymer exchangers for a better understanding of the separation processes.

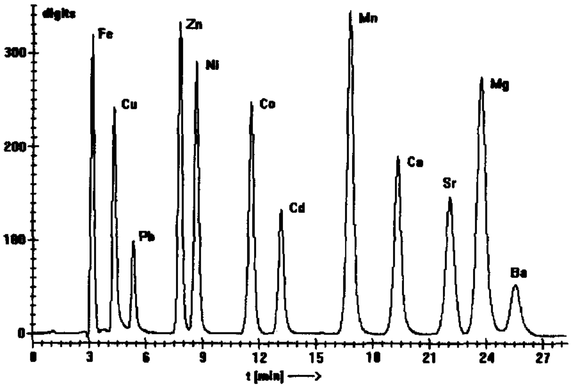

Fig. 1. Separation of twelve ions on a 300 mm × 4 mm I.D. Nucleosil 5SA column under optimized operating conditions [0.1 M tartrate (pH 3.3, adjusted with NH_3), flow-rate 1.0 ml/min].

For division of the elution behaviour of the tartaric acid–base system into a complexation-dominated part and a counter ion elution part, the selectivity coefficients for the polymer exchangers were evaluated with nitric acid as a protic eluent. This allows a comparison of the selectivity coefficients in acid and in complexing eluents.

EXPERIMENTAL

Column packings

The macroporous PS–DVB copolymers used in this work for the preparation of partially sulphonated ion exchangers were commercially available beads (RoGel SEC and RP) distributed by Bio-Rad Labs. (Munich, Germany). Their common application is in organic size-exclusion or reversed-phase chromatography. The degree of cross-linking is very high in order to guarantee HPLC conformity. The silica-based cation exchanger RoSil CAT was also obtained from Bio-Rad Labs. The widely used silica-based cation exchanger Nucleosil 5SA was supplied by Macherey–Nagel (Düren, Germany). All materials have an average core diameter of 5 μm and their general physical properties are given in Table I.

Sulphonation of polystyrene

The sulphonation of PS–DVB beads has been widely described [12–20]. The following procedure was finally used to produce homogeneous cation-exchange resins.

A 20-ml volume of concentrated sulphuric acid (96%) was placed in a 50-ml reaction vessel. After the addition of 0.1 g of silver sulphate as sulphonation catalyst the mixture was warmed to the desired reaction temperature. The catalyst was dissolved only by mechanical shaking. A portion of 1 g of dry resin was transferred to the reaction vessel and ultrasonically dispersed. The colour of the reaction mixture immediately turned from slightly yellow to dark brown. The beads were sulphonated for various reaction times (30 min–3 h) and at temperatures ranging from 0 to 87°C (see Table II). The reaction was quenched by removal of the liquid by filtration.

TABLE I

PHYSICAL PROPERTIES OF THE UNMODIFIED RESINS

Physical properties	RoGel SEC	RoGel SEC	RoGel RP	Nucleosil	RoSil
Particle size (μm)	5	5	5	5	5
Cross-linking	Very high	Very high	Very high	–	–
Maximum pressure (MPa)	20	20	20	60	80
Mean pore size, $d_{\mathrm{p}50}$ (nm)	3	7	7	10	9
Maximum pore size, $d_{\mathrm{p}10}$ (nm)	11	40	No specification	No specification	No specification
Surface area (m^2/g)	500	450	450	350	250
Pore volume (ml/g)	0.67	1.30	1.30	1.0	0.65
Maximum diameter, $d_{\mathrm{p}10}$ (nm)	No specification	7	7	6.5	6
Minimum diameter, $d_{\mathrm{p}10}$ (nm)	No specification	3	3	3.5	4

The resin was then suspended in 9 *M* H_2SO_4 to prevent breakage of the cores by sudden contact with aqueous solutions. After removal of the excess of sulphuric acid, the beads were washed in sequence with 3 *M* HCl, water, ethanol, water, 2 *M* ammonia solution, water and 1 *M* HCl. Subsequently the materials were refluxed with water for complete removal of residual acid. The grey to slightly brown products were filtered, dried and characterized [15,16,19,21]. A slurry technique was used for column packing of polymeric and silica-based materials.

TABLE II

SULPHONATION CONDITIONS AND OBSERVED CAPACITIES FOR DIFFERENT PS–DVB COPOLYMERS

Material	Reaction time (h)	Reaction temperature (°C)	Specific capacity (H^+) (mmol/g)
RoGel SEC (3 nm)	1	65	1.55
	1	30	0.72
	1	10	0.61
	1/2	0	0.34
RoGel RP (7 nm)	1	87	1.95
	1	0	0.45
	1/2	0	0.36
RoGel SEC (7 nm)	3	67	1.76
	1/2	0	0.34

Evaluation of the selectivity coefficient against H^+

The selectivity coefficients for several sample ions were determined with 4, 3, 2, 1, 0.5, 0.25 and 0.125 *M* nitric acid as eluents and inductively coupled plasma spectrometry (ICP-AES) for element-specific detection (simultaneous working type from Spectro A.I., Kleve, Germany). The instrumentation has been described in detail elsewhere [22].

Instrumentation

The HPLC system consisted of a Type 64 HPLC-pump (Knauer, Berlin, Germany), a pneumatic injection valve (Knauer) with a 20-μl sample loop, a Type 87.00 variable-wavelength detector and 100 mm × 4 mm I.D. stainless-steel columns (Vertex) as analytical column. Postcolumn detection of the ions was effected by reaction with 4-(2-pyridylazo) resorcinol (PAR), Zn–EDTA ($0.25 \cdot 10^{-4}$ *M* Zn–EDTA, $1 \cdot 10^{-4}$ *M* PAR, 2 *M* NH_3). The postcolumn reagent was added to the eluate in the postcolumn reactor by a single-piston HPLC pump (LDC Analytical). The absorbance of the eluate was monitored at 495 nm. The overall system control and the readout of the detector were processed by a computer system.

Reagents

All reagents were of high purity and standard solutions of the inorganic cations were prepared using 1000 mg/l stock standard solutions. Aliquots of these stock standard solutions were used to prepare cation mixtures containing the ions to be investigated in a range 2–60 mg/l.

Eluent preparation

All eluents were prepared with tartaric acid (Fluka, microselect quality) and water purified with a Milli-Q system (Millipore) with a minimum resistivity of 18 MΩ. The pH was adjusted with 4 *M* NaOH (Merck, analytical-reagent grade, maximum 0.0002% K^+). The concentration of the eluents ranged from 0.1 to 0.25 *M* tartaric acid and their pH from 2.7 to 3.96.

To prepare a dynamically coated ion exchanger from the unmodified PS–DVB resins, 0.005 *M* dodecyl sulphonate solution was passed through the column until equilibration was achieved. The mobile phase was then changed to tartrate containing 0.002 *M* dodecyl sulphate to maintain the coating [23].

RESULTS AND DISCUSSION

Table III shows an overview of the exchangers investigated. The prepared polymer exchangers have volume capacities comparable to those of commercial silica gel-based exchangers.

Sulphonation behaviour of RoGel

The capacities of the sulphonated beads are given in Table II as function of reaction time and temperature. The capacities of the sulphonated resins are easily adjustable in the range 0.3–0.7 mmol/g and increase with increasing reaction temperature and time. The temperature is more important than the reaction time for the observed capacity, hence the temperature should be selected very carefully. The capacity $Q(H^+)$ of 2 mmol/g seems to be the maximum sulphonation grade possible with 96% sulphuric acid for these resins. Attempts to obtain higher capacities resulted in increasing breakage of the beads (Fig. 2).

No differences in the sulphonation behaviour could be determined for RoGel SEC and RoGel RP. The capacities reported [13,17] under similar sulphonation conditions as chosen are not comparable for low-cross-linked PS–DVB. The large surface area of the macroporous RoGel results in faster sulphonation of the core. Therefore, it can be assumed that the sulphonation is controlled by the surface area of the beads.

Selectivity coefficients in nitric acid

The fundamental exchange characteristics of a cation exchanger could be investigated with a

TABLE III

DESCRIPTION OF THE COLUMNS USED

Column	Short name	Surface sulphonated	Volume capacity (H^+) (mmol/ml)	Specific capacity per gram of resin (H^+) (mmol/g)
RoGel SEC (7 nm)	RoS7-34	Yes	0.135	0.34
RoGel RP (7 nm)	RoR7-36	Yes	0.142	0.36
RoGel SEC (3 nm)	RoS3-34	Yes	0.183	0.34
RoGel SEC (3 nm)	RoS3-61	Yes	0.301	0.61
RoGel SEC (7 nm)	RoS3-72	Yes	0.366	0.72
RoGel RP dodecyl sulphate	RoR7-Do			–
Nucleosil 5SA	Nucl-SA		0.151	
RoSil CAT (5 μm)	Rosil		0.374	
Only for H^+ measurements:				
RoGel RP (7 nm)	RoR7-45	Yes	0.117	0.45
RoGel SEC (3 nm)	RoS3-155	Yes	0.678	1.55
RoGel SEC (7 nm)	RoS7-176	Yes	0.701	1.76
RoGel RP (7 nm)	RoR7-195	Yes	0.838	1.95
AG 50W-X8 (< 400 mesh)	50W-X8	Yes	1.86	5.1
AG 50W-X16 (200–400 mesh)	50W-X16	Yes	2.02	5.1

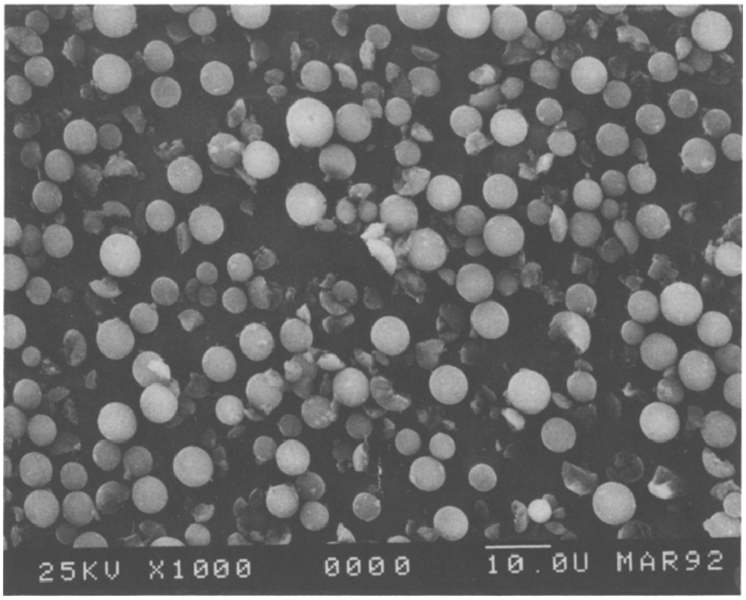

Fig. 2. Breakage of the RoGel PS–DVB cores obtained for high sulphonation grades.

strong acid as protic eluent. In this work nitric acid was used because of its low complexation tendency.

The affinity of a cation to a cation exchanger is normally described by the selectivity coefficient K_M^E, which is defined as the equilibrium constant of the ion-exchange reaction

$$n\,E^+R + M^{n+} \rightleftharpoons M^{n+}R_n + n\,E^+ \tag{1}$$

where E^+ is usually a monovalent eluent cation (in this study hydrogen or sodium), M^{n+} is the sample metal ion and R represents the cation exchanger. The term $[M^{n+}R_n]$ means the concentration of the analyte fixed at the exchange group. The selectivity coefficient for this reaction is

$$K_M^E = \frac{[M^{n+}R_n]\,[E^+]^n}{[E^+R]^n\,[M^{n+}]} \tag{2}$$

At low loading of sample ions, the term $[E^+R]$ is approximately equal to the resin capacity Q_v. The ratio $[M^{n+}R_n] / [M^{n+}]$ is given by the capacity factor k'. All terms in square brackets are volume concentrations. A plot of the product of the capacity factor and the reciprocal of resin capacity (volume capacity) *versus* the reciprocal of the square or cube (depending on the sample ion charge) of the eluent cation concentration gives as the slope the selectivity coefficient:

$$k'\,[Q_v]^{-n} = K_M^E \cdot [E^+]^{-n} \tag{3}$$

The selectivity coefficients for a number of ion-exchange resins are given in Table IV. The classical ion exchangers AG 50W-X8 and -X16 were investigated as references. Those resins are fully sulphonated and the observed selectivity coefficients are taken as a standard value for the selectivity caused only by ion exchange. The other exchangers are based on macroporous PS–DVB and have an increasing exchange capacity from 0.1 to 0.85 mmol/ml.

For ions with a high exchange density such as Mg^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+} the selectivity coefficient is nearly independent of both the resin capacity and porosity. This behaviour is more evident for trivalent cations. Copper shows no dependence on resin capacity. More polarizable cations such as Cd^{2+}, Mn^{2+} and the alkaline earth metals Ca^{2+} and Ba^{2+} show a increasing selectivity coefficient with increasing capacity. The univalent K^+ ion shows a similar behaviour. The increase in the selectivity coefficient could be explained by adsorption.

TABLE IV

SELECTIVITY COEFFICIENT FOR VARIOUS CATION EXCHANGERS OBTAINED WITH NITRIC ACID ELUENTS

Element	Charge	Selectivity coefficient (K^E_M) for H^+						
		RoR7-45 (0.117)[a]	RoS3-61 (0.301)[a]	RoS3-155 (0.678)[a]	RoS7-176 (0.701)[a]	RoR7-195 (0.838)[a]	AG 50W-X8 (1.86)[a]	AG 50W-X16 (2.02)[a]
Al	3	27	15	9.6	8.9	7.5	10	10
Fe	3	60	54	36			14	13
Cr	3	28	19	11	12	9.6	11	11
Mg	2	2.6	2.0	1.9	2.2	1.9	2.6	2.7
Ca	2	4.4	11	15	25	28	5.1	7.4
Ba	2	12	25	38	67	78	13	14
Cu	2	3.6	3.7	3.9	4.6	4.0	3.0	3.4
Zn	2	2.9	2.6	2.65	3.1	2.7	2.9	2.3
Ni	2	2.9	2.5	2.5	2.8	2.4	3.0	2.1
Co	2	2.9	2.6	2.6	3.1	2.6	3.1	2.2
Cd	2	3.8	5.4	5.7	6.8	8.8	2.8	3.3
Mn	2	3.3	3.8	4.4	6.0	5.7	3.4	4.0
Pb	2	21	63	26	65	42	7.2	7.7
K	1	0.7	1.5	4.1	4.8	8.4	2.8	4.5
Na	1	0.5	0.5	1.13	1.5	2.1	1.3	1.6

[a] Volume capacity (mequiv./ml).

It should be noted that the extent of this non-specific interaction is correlated with the capacity of the resin.

Pb^{2+} always shows a higher selectivity coefficient on partially sulphonated macroporous resins than on the classical fully sulphonated microporous resins. The exchange group $-SO_3^-$ seems to be necessary to lower the distance between the sample ion and the residual hydrophobic surface of a partially sulphonated macroporous resin and therefore permits adsorption.

The selectivity coefficients for Al^{3+}, Fe^{3+} and Cr^{3+} ions are decrease strongly with increasing resin capacity. The values for high-capacity macroporous resins are similar to the values obtained for the microporous AG 50W exchangers. The extremely high selectivity coefficients at low capacities are probably caused by the large distance between the exchange sites, which does not allow interaction with the stochiometrically needed three $-SO_3^-$ groups.

Tartaric acid–base elution system

Elution systems for heavy and transition metals consists of a complexing reagent and a singly or doubly charged cation, which is normally delivered from the pH-adjusting base. The complexing reagent must be weak for a cation exchanger, otherwise the sample ion is fully complexed and no longer retained by cation exchangers. Most common complexing reagents are hydroxycarboxylic acids such as tartaric or citric acid. The elution mechanism is a combination of the mass action effect of the eluent cation and complexation of the sample ion, which lowers the actual sample ion concentration that interacts with the exchange sites.

Tartaric acid is a dibasic acid with close pK values. For a total ion strength of 0.1, $pK_{a_1} = 2.92$ and $pK_{a_2} = 4.09$ [26]. The greatest changes in the complexation behaviour should be obtained at pH values below pK_{a_1}; smaller changes should be obtained between pK_{a_1} and pK_{a_2}. The pH range between pK_{a_1} and pK_{a_2} was investigated in this work.

For a theoretical description of a complexing eluent, a factor α_M is defined [24,25], which represents the ratio between non-complexed and complexed sample ions in the solution:

$$[M'^{n+}] = \frac{[M^{n+}]}{\alpha_M} \qquad (4)$$

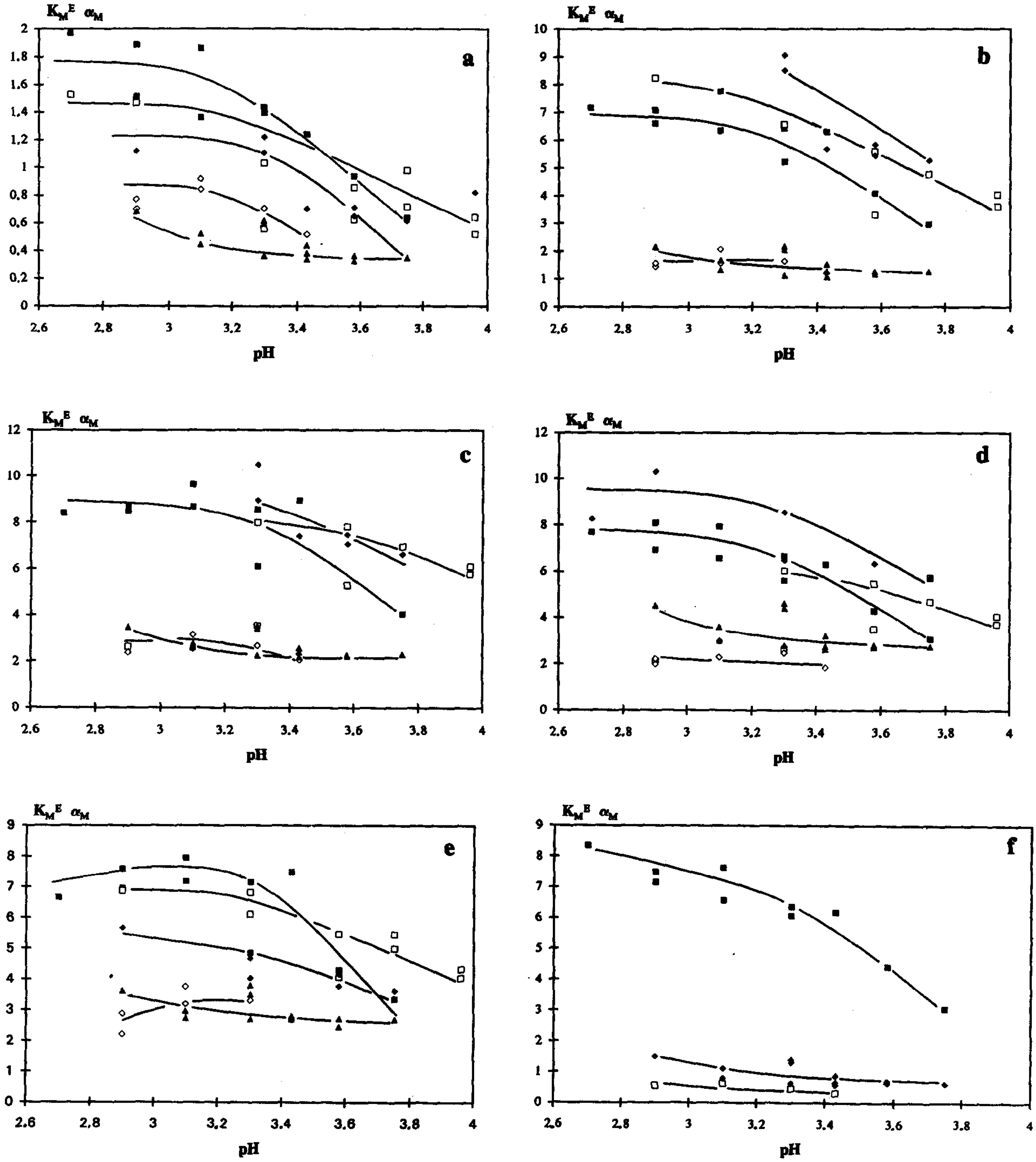

Fig. 3. Plot of the product of the selectivity coefficient, K^E_M, and the fraction of the uncomplexed sample ions in the solution, α_M, *versus* the pH of the tartrate eluent for (a) Zn, (b) Cd, (c) Mn, (d) Ca, (e) Mg and (f) Pb. (a–e) ■ = RoR7-34; □ = RoS3-61; ◆ = RoS3-72; ◇ = Nucl SA; ▲ = RoSil. (f) ■ = RoR7-34; □ = Nucl SA; ◇ = RoSil.

The modified eqn. 2 is now

$$K_{\mathrm{M}}^{\mathrm{E}} = \frac{[\mathrm{M}^{n+}\mathrm{R}_n]\,[\mathrm{E}^+]^n}{[\mathrm{E}^+\mathrm{R}]^n\,[\mathrm{M}'^{n+}]\alpha_{\mathrm{M}}} \qquad (5)$$

or, with $k' = [\mathrm{M}^{n+}\mathrm{R}_n] / [\mathrm{M}^{n+}]$,

$$k'Q_{\mathrm{v}}{}^{-n}\,[\mathrm{E}^+]^n = K_{\mathrm{M}}^{\mathrm{E}}\,\alpha_{\mathrm{M}} \qquad (6)$$

A plot of $k'\,[Q_{\mathrm{v}}]^{-n}\,[\mathrm{E}^+]^n$ *versus* the pH of the eluent allows the product of the selectivity coefficient and α_{M} to be obtained. The α_{M} value should be constant for a given pH value, whereas differences between the $K_{\mathrm{M}}^{\mathrm{E}}$ values are obtained. On the other hand, the $K_{\mathrm{M}}^{\mathrm{E}}$ value should be constant for a given exchanger and a change in α_{M} caused by as pH change is obtained.

Fig. 3a–f show such diagrams for selected sample ions. Some ions such as the less polarizable Zn^{2+}, Ni^{2+},Co^{2+} and Mg^{2+} show only small differences between silica gel and polymeric exchangers. The polymeric exchangers generally have higher selectivity coefficients with an increasing tendency towards lower exchange capacities. This agrees with the behaviour of these ions against protic eluents.

The less polarizable Mn^{2+} ion shows a smaller increase in the selectivity coefficient with increasing resin capacity for surface-sulphonated exchangers than Cd^{2+}, Ca^{2+} and Pb^{2+} ions. This behaviour is not obvious for dynamically coated exchangers and for silica gel-based exchangers with their different exchange site structure. A detailed discussion of the effects is given later.

Comparison of polymer- and silica gel-based exchangers

Significant differences between silica gel and polymeric exchangers are the hydrophobicity of the substrate and the position of the functional group. The silica gel exchangers Nucleosil SA (n = 3) and RoSil CAT (n = 1) have an $\mathrm{R(CH_2)}_n\mathrm{C_6H_4SO_3H}$ group, whereas the sulphonic acid group of the polymeric exchangers is directly attached to the PS–DVB substrate. The HETP values (Table V) show the variation in performance with the sulphonic acid group location. The HETP values for silica gel exchangers are lower than those obtained for the polymer-based exchangers.

Division of the performance difference between surface-sulphonated exchangers and those with a distance between the exchange site and substrate into particle size distribution-dominated and exchange site structure-dominated parts is possible be generation of a dynamically coated exchanger based on the same substrate as the surface-sulphonated exchangers. The even lower HETP values for silica gel exchangers than observed for the dynamically coated exchanger are caused by the narrower particle size distribution, which is a typical advantage of silica gel substrates. It is not possible to produce PS–DVB exchangers at this quality level.

The observed changes in HETP for Mg as a late-eluting ion with no adsorption tendency are caused only by the slower mass transfer at the exchange site. Other elements such as Pb, Cd and Mn show

TABLE V

HETP VALUES (mm) FOR VARIOUS IONS UNDER THE SAME CHROMATOGRAPHIC CONDITIONS (0.175M TARTARIC ACID, pH 3.3 WITH NaOH) FOR DIFFERENT EXCHANGERS

Column	Zn^{2+}	Ni^{2+}	Co^{2+}	Cd^{2+}	Mn^{2+}	Ca^{2+}	Mg^{2+}	Pb^{2+}
RoGel SEC (7 nm, 0.34 mmol H^+/g)	0.20	0.23	0.14	0.24	0.20	0.16	0.14	1.47
RoGel RP (7 nm, 0.36 mmol H^+/g)	0.17	0.23	0.14	0.23	0.17	0.15	0.14	1.28
RoGel SEC (3 nm, 0.34 mmol H^+/g)	0.28	0.32	0.29	0.34	0.28	0.28	0.20	1.36
RoGel SEC (3 nm, 0.61 mmol H^+/g)	0.30	0.35	0.28	0.28	0.25	0.27	0.15	2.62
RoGel SEC (7 nm, 0.72 mmol H^+/g)	0.34	0.42	0.23	0.28	0.44	0.21	0.19	>3
RoGel RP dodecyl sulphate	0.12	0.14	0.11	0.11	0.11	0.16	0.084	0.315
Nucleosil 5SA	0.095	0.085	0.065	0.063	0.051	0.044	0.048	0.12
RoSil CAT (5 μm)	0.04	0.045	0.026	0.025	0.017	0.015	0.017	0.25

increased HETP values for the surface-sulphonated exchangers caused by an increase in the non-specific interaction with the polymer surface. The differences between the HETP values of elements with comparable retention times on surface-sulphonated exchangers such as Mg and Pb cannot be explained by different locations of the exchange groups such as *ortho-* and *para-*sulphonic acid groups [2]. For Pb the non-specific interaction seems to be an important part of the separation process.

The performance of RoSil CAT is nearly one order of magnitude better than those of surface-sulphonated resins; compared with Nucleosil SA there is a 2–4-fold better performance. On the one hand the chromatographic performance of RoSil CAT is excellent, but on the other the selectivity is not sufficient for the separation of Pb and Co or of Mn and Mg using the tartaric acid elution system (Fig. 4).

Resolution of selected sample ion pairs

The resolution of selected ion pairs is discussed with the help of the separation factor α as defined by

$$\alpha_{A/B} = k'_A / k'_B \tag{7}$$

Zn–Ni. These ions are normally not completely separated with surface-sulphonated polymeric exchangers using the tartaric acid elution system. Only silica gel-based exchangers and the dynamically coated exchangers are able to separate these ions. The selectivity data obtained are given in Table VI.

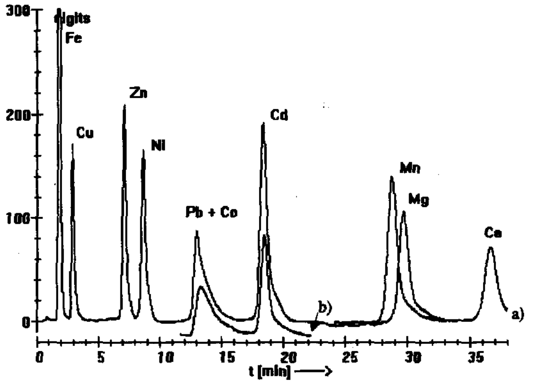

Fig. 4. Typical chromatogram obtained with RoSil CAT for a 100 × 4 mm I.D. column with 0.25 *M* tartrate (pH 2.9, adjusted with NaOH) and with a flow-rate of 1.0 ml/min. The overlaid chromatogram (b) shows the Pb peak without Co overlap.

TABLE VI

SELECTIVITY OBSERVED FOR Zn–Ni FOR DIFFERENT EXCHANGERS OBTAINED WITH 0.1–0.25 *M* TARTARIC ACID WITH pH RANGING FROM 2.7 TO 3.96 (ADJUSTED WITH NaOH) AND FOR THE PAIR Ni–Co AT A FIXED pH OF 3.3 AND 0.175 *M* TARTARIC ACID

Column	$\alpha_{Zn/Ni}$		$\alpha_{Ni/Co}$
	Value	R.S.D.[a] (%)	
RoGel SEC (7 nm, 0.34 mmol H^+/g)	1.11	2.6	1.88
RoGel RP (7 nm, 0.34 mmol H^+/g)	1.09	5.8	1.85
RoGel SEC (3 nm, 0.34 mmol H^+/g)	1.08	3.5	2.03
RoGel SEC (3 nm, 0.61 mmol H^+/g)	1.03	4.8	1.98
RoGel SEC (7 nm, 0.72 mmol H^+/g)	0.93	3.1	2.06
RoGel RP dodecyl sulphate	1.25	2.3	1.71
Nucleosil 5SA	1.19	2.4	1.45
RoSil CAT (5 μm)	1.28	3.7	1.70

[a] $n = 10$.

The low relative standard deviation (R.S.D.) of the observed selectivity over a wide pH range and for three different tartrate concentrations suggests that the resolution is independent of pH and eluent concentration. This is caused by the similar selectivity coefficients (Table IV) and the similar complexation behaviour of the two ions. For polymeric resins the selectivity is dependent on the resin capacity with an inversion point near 0.3 mmol/ml resin capacity (Table VI).

Ni–Co. These ions have very similar selectivity coefficients (Table IV); their separation is mainly caused by differences in their complexation behaviour. The selectivity generally increases with increasing pH; Fig. 5a displays two typical graphs for $\alpha_{Ni/Co}$ *vs.* pH. The offset between the different tartaric acid concentrations is probably caused by small differences in the selectivity coefficients against the sodium ion. This explains the tendency shown in Table VI for the different packing materials. $\alpha_{Ni/Co}$ is generally higher for surface-sulphonated PS–DVB packings than for modified silica gel or the dynamically coated exchanger.

Co–Cd. The selectivity coefficient for Cd increases strongly with increasing resin capacity. This dependence is similar for H^+ (Table IV) and Na^+ (Fig. 3b) as eluent cation. This is not evident for silica gel-based exchangers, whereas the selectivity

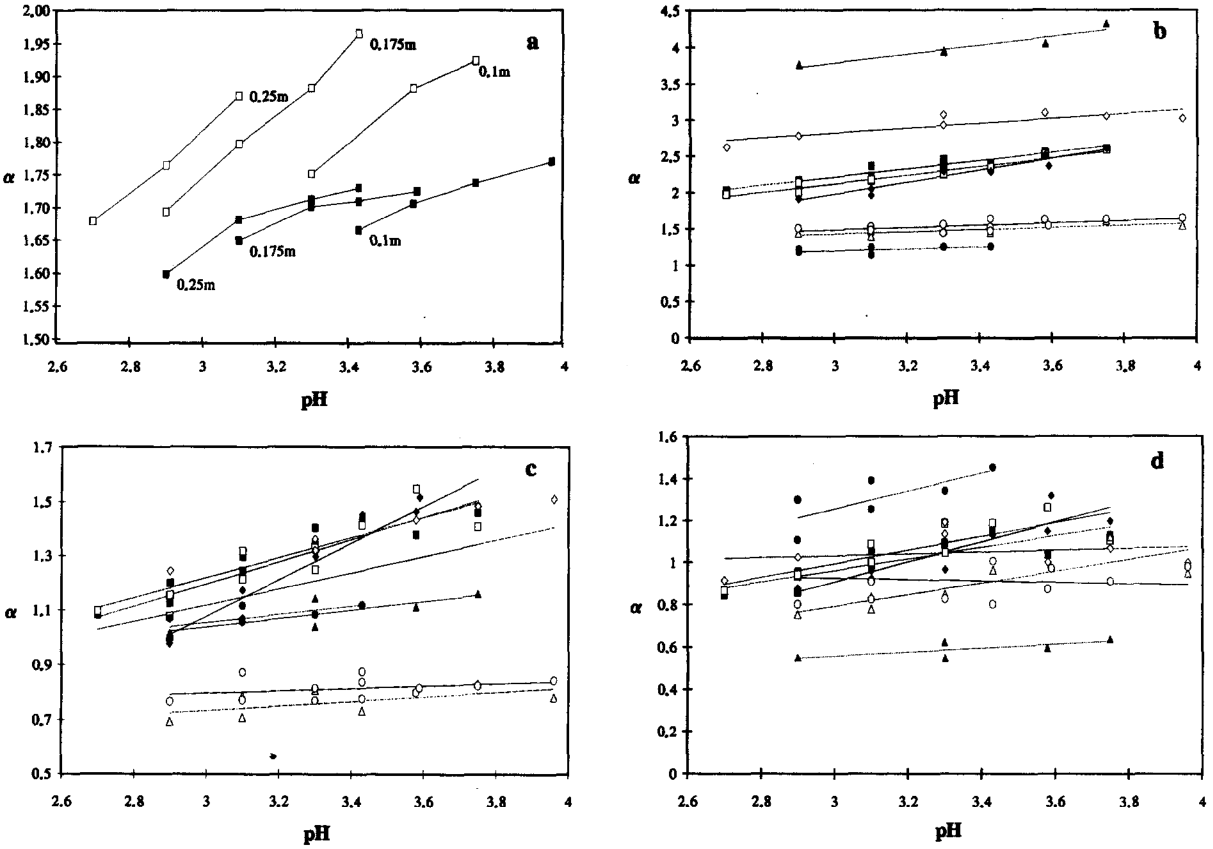

Fig. 5. Plot of the separation factor, α, *versus* pH for the ion pairs (a) Ni–Co, (b) Co–Cd, (c) Ca–Mn and (d) Ca–Mg. (a) ■ = Rosil; □ = RoS7-34. (b–d) ■ = RoS7-34; □ = RoR7-36; ◆ = RoS3-34; ◇ = RoS3-61; ▲ = RoS3-72; △ = RoR7-Dodec; ● = Nucl SA; □ = Rosil.

coefficients are nearly independent of resin capacity (Fig. 3b). The Co^{2+} ion shows only a small dependence of the selectivity coefficient with an increase with decreasing capacity. The separation of the two ions is difficult only with silica gel-based exchangers; in comparison, the surface-sulphonated exchangers show selectivities ranging from 2 to 4 with an increase with increasing resin capacity (Fig. 5b). This is caused by the dominating increase of the selectivity coefficient for Cd. It should be noted that the behaviour of both ions is very similar on RoSil CAT and on the dynamically coated exchanger.

Ca–Mn. The separation of Ca and Mn is a difficult task with Nucleosil SA. Fig. 5c shows that both the higher capacity RoSil CAT and the dynamically coated exchanger with a similar capacity to RoSil CAT and also the surface-sulphonated exchangers permit a better separation of these ions RoSil CAT and the dynamically coated exchanger show an inverse elution order, Mn being eluted before Ca. This behaviour is caused by the different selectivity coefficients for Ca and Mn. This is the main effect which leads to the better separation observed for surface-sulphonated exchangers. Table IV and Fig. 3e and f show a small difference between the selectivity coefficients at low functionalization grades and a rapid increase for Ca with increasing capacity. For Mn only a small increase in the selectivity coefficient is observed. When the selectivity coefficients are nearly equal, the more stable Ca–tartaric acid complex {log β_1 (Ca–tart) = 1.7 [26]; log β_1 (Mn–tart) = 1.44 [27]} is dominant for the good

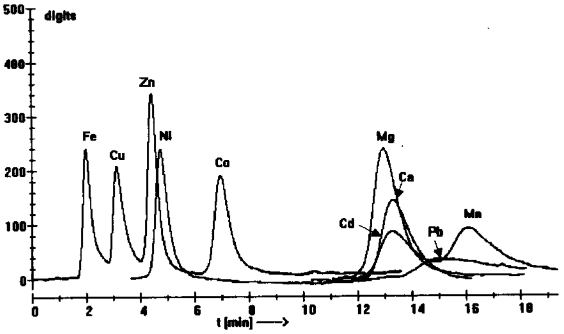

Fig. 6. Overlay of several chromatograms obtained with RoS7-34 for a 100 × 4 mm I.D. column with 0.175 *M* tartrate (pH 3.1, adjusted with NaOH) with a flow-rate of 1.0 ml/min.

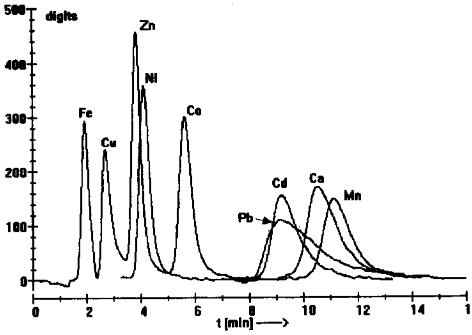

Fig. 7. Overlay of several chromatograms obtained with RoS3-61 for a 100 × 4 mm I.D. column with 0.25 *M* tartrate (pH 2.9, adjusted with NaOH) with a flow-rate of 1.0 ml/min.

separation of these ions. At higher resin capacities this different complexation behaviour is compensated for by the rapidly increasing selectivity coefficient for Ca.

Ca–Mg. Between these ions large differences in the complexation behaviour and in the selectivity coefficients are observed. Mg is only slightly complexed by tartrate, the elution being dominated by the mass action of the eluent cation. On the other hand, Ca forms stable tartrate complexes similarly to the Mn^{2+} ion.

Fig. 3e shows the dependence of the α_M value on pH for Mg and Fig. 3d that for Ca. The tendency is the same for both ions, but only for Ca is a significant difference between the two silica gel exchangers observable, which means that a dependence of the selectivity coefficient on the capacity of the exchanger is evident. This is in good agreement with the results of selectivity coefficient evaluations in nitric acid solutions (Table IV). The selectivity coefficients observed for surface-sulphonated resins increase with sodium as eluent cation for Mg with decreasing resin capacity; the behaviour of Ca is the opposite. This agrees with the selectivity coefficients obtained for H^+ as eluent cation.

The separation of Ca and Mg is strongly dependent on eluent pH, the separation factor increases for all resins with increasing pH. Only for the high-capacity surface-sulphonated resins and RoSil CAT does the separation factor for Ca and Mg decrease with increasing pH. On the other hand, the separation factor increases for low-capacity polymeric exchangers and for Nucleosil SA. Between these capacities the separation factor for Ca / Mg is very close to one and their separation is possible only with a high-performance column.

This tendency is also shown in Fig. 5d; the increasing separation factor is caused by an increase in complexation of the Ca^{2+} ion. The best resolution is obtained for the low-capacity Nucleosil SA with elution of Ca before Mg and for the highest capacity surface-sulphonated exchanger with an inverse elution order.

Pb. Lead is the sample ion with the greatest difference between the behaviour on silica gel- and polymer-based exchangers. It forms a relatively stable tartaric acid complex and has an extremly high selectivity coefficient. The higher the exchange capacity of the resin, the higher is the selectivity coefficient for lead. On surface-sulphonated polymeric resins an extremely high degree of adsorption is observed. At pH values higher than 3.1 Pb is eluted directly after Cd; below pH 3.1 Pb is eluted after Mg.

On Nucleosil SA Pb is eluted early between Cu and Zn. On RoSil CAT Pb is eluted closely after Co and on the dynamically coated exchanger just before Co. A sulphonic exchange group at a distance from the substrate lowers the selectivity coefficient for Pb. In addition, the HETP value decreases by nearly one order of magnitude.

CONCLUSIONS

The chromatographic performance of surface-sulphonated exchangers is in all instances well below the performance obtained with silica gel exchangers (Figs. 1 and 4 compared with Figs. 6 and 7; Table 5). The use of modern PS–DVB substrates leads to a performance one order of magnitude below the standard set by the RoSil CAT exchanger. With elimination of the influence of different particle size distributions by generation of a dynamically coated exchanger, the performance is approximately five fold below that of Rosil CAT. This leads to the conclusion that the structure of the exchange site is extremely important for the chromatographic performance. Only a sulphonic acid group that is not directly attached to the substrate permits optimum performance.

The surface-sulphonated resins show substantial non-specific interaction for polarizable ions. This results for lead, for example, in poor performance with HETP values of 1.2–3 mm. The influence of adsorptive interactions on the selectivity coefficient increases with increasing resin capacity. This could be explained with help of the hydrophobic character of the substrate, which is only lowered at locations with a sulphonic acid group. A cation with a hydrophilic water cloud in the wider coordination sphere will only interact with the π-system of the core if the distance between the core and the polarizable cation is lowered by ion attraction of the exchange group.

In general, the selectivity coefficients increase at low capacities, which probably arise when the distance between the stochiometrically needed exchange sites becomes to great. This point is reached for trivalent cations at even higher volume capacities than for divalent cations.

The dynamically coated exchanger shows an exchange behaviour very similar to that of the silica gel-based RoSil CAT exchanger. The two silica gel-based exchangers show different selectivities owing to their different capacities, whereas the capacity of Nucleosil SA seems to be the optimum for the separation system investigated. The higher chromatographic performance of RoSil CAT is insufficient to solve separation problems caused by poorer selectivity characteristics for this elution system.

ACKNOWLEDGEMENTS

The authors thank G. Wünsch for his support of this work and R. Krismer of Metallwerk Plansee for the SEM pictures.

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