Ion-chromatographic selectivity of polyelectrolyte sorbents based on some aliphatic and aromatic ionenes

A.V. Pirogov*, O.V. Krokhin, M.M. Platonov, Ya.I. Deryugina, O.A. Shpigun

Moscow State University, Chemistry Department, GSP-3, Lenin Hills, 119899 Moscow, Russia

Abstract

An aliphatic ionene with hydroxyl group (2HP-8 ionene), mixed aliphatic–aromatic ionenes (3-X and 6-X ionenes), aromatic ionene (Ph-X ionene), and viologen (Dp-X ionene) – polymers with quaternary nitrogen atoms in the main chain – served as modifiers in synthesising polyelectrolyte sorbents for ion chromatography. The selectivity of produced and several previously prepared anion exchangers was compared with those of aliphatic ionenes. It was found that aromatic ionenes having a rigid structure of polymer chains are similar to their aliphatic analogues with shorter chains with a high charge density. Polyelectrolyte sorbents based on aromatic ionenes show higher selectivity to aromatic acids (e.g., 1-naphthalenesulfonic acid) as compared with aliphatic ionenes due to specific $\pi-\pi$ interactions.   © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, LC; Polyelectrolyte sorbents; Ionenes

1. Introduction

Synthesising sorbents for ion chromatography is a sophisticated task because many requirements are imposed, like low ion-exchange capacity, small particle size, and mechanical and chemical stability. A promising approach for preparing efficient anion exchangers is modifying hydrophobized silica or other suitable matrices with polyelectrolyte complexes formed as a result of heterogeneous interaction between anion-active compounds and polycations [1–3]. From this point on, we will refer to these materials as "polyelectrolyte sorbents" (although this name has some drawbacks). Such an approach for preparing sorbents provides the possibility of varying the selectivity over a wide range by changing the structure of functional groups in the polyelectrolyte complex. Moreover, this approach decreases the cost of anion exchangers and synthesis time. In our previous paper [3] we investigated in detail the selectivity of anion exchangers produced with the use of aliphatic ionenes as modifiers. As a result, we divided the produced ion exchangers into three groups.

Compared to aliphatic ionenes, their aromatic analogues are characterised by several specific properties. Firstly, specific $\pi-\pi$ interactions between the sorbent and the sorbate are possible. Secondly, aromatic ionenes are more hydrophobic, but have a rigid linear structure. Such differences allow us to suppose that selectivity of ion exchangers based on aromatic ionenes would differ from their aliphatic analogues. The aim of this study was to synthesise polyelectrolyte anion exchangers using water-soluble

*Corresponding author. Tel.: +7-095-9394-608; fax: +7-095-9394-675.

E-mail address: pirogov@analyt.chem.msu.ru (A.V. Pirogov)

polymers of aromatic ionene type as modifiers and to compare their selectivity with that of previously synthesised materials.

2. Experimental

2.1. Instrumentation and chemicals

A chromatographic system equipped with a Shimadzu LC-10AD pump (Shimadzu, Japan), a BT-8200 spectrophotometric detector (Eppendorf-Netheler Hinz, Division Biotronik, Germany) with tuneable wavelength was used throughout. Indirect UV detection at 254 nm was used. Stainless steel columns (50×3 mm) were used. Injected sample volume was 50 μl. Flow-rate was 1 ml/min. An integrator C-R3A (Shimadzu, Japan) served for the recording of chromatograms. The "Silasorb-S" (5 μm, Lachema, Brno, Czech Republic) reversed-phase silica with chemically-bonded sulfo groups was used for the synthesis of the packing materials as major matrix. We also used Kahk-CSt (10 μm, Moscow, Russia), styrene–divinylbenzene cation exchanger, and AG 50W-X2 (25–30 μm, Bio-Rad, USA) styrene–divinylbenzene cation exchanger. Deionised water was obtained from a Barnstead Fstreem III water purification system (UK). It was used for preparing all the solutions.

N,N,N',N'-Tetramethyl-1,3-diaminopropane, $N,N,$-N',N'-tetramethyl-1,6-hexanediamine, 1,3-bis(dimethylamino)-2-propanol and 4,4'-dipyridyl were obtained from Aldrich (Steinheim, Germany). N,N,N',N'-Tetramethylethylenediamine was obtained from ICN Pharmaceuticals (Costa Mesa, CA, USA); N,N,N',N'-tetrametyl-p-phenylenediamine dihydrochloride was obtained from Sigma (St. Louis, MO, USA); α,α'-dibromo-p-xylene was obtained from Wako (Osaka, Japan). Solvents [acetone, dimethylformamide (DMF)] were spectral grade and used without further purification.

2.2. Synthesis of ionenes

Ionenes are polymers with quaternary nitrogen atoms in the backbone. The range of substances that fulfil this definition is wide. In this study we consider polyammonium salts, which are most commonly called ionenes. Aromatic ionenes are also called viologens. The term "ionenes" was introduced by Rembaum et al. in 1968 [4]. In the last years more than 200 papers and patents devoted to the synthesis and properties of new ionenes and viologens have been published [5–15].

The most widespread method for synthesising ionenes is a multiple Menshutkin reaction (N-alkylation) [16]:

$$(1)$$
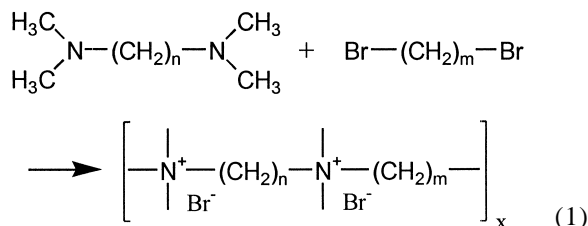
We used this reaction for synthesising all ionenes and viologens. The following description illustrates the method used in the synthesis of 3-X, 6-X, Ph-X, Dp-X and 2HP-8 ionenes (Table 1). It should be noted that Dp-X polymer is an oxidation–reduction chromophore and under photoirradiation, produces a viologen cation-radical, accompanied by a colour development:

viologen dication

viologen cation radical

$$(2)$$
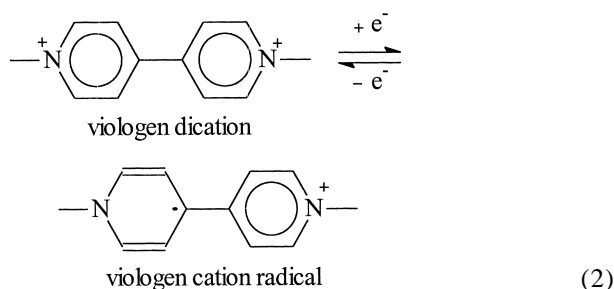
The anion-exchange capacity for Dp-X modified sorbents is about twofold less than those for other polyelectrolyte packing materials. Apparently, the reason for this phenomenon is the decrease in the amount of positively-charged nitrogen atoms in molecule of Dp-X by Eq. (2).

The polymerisation was carried out in a DMF solution using equimolar monomers at room temperature. The total concentration of monomers was 1.0 mol/l and the reaction time was 0.5–30 h (depending on the activity of diamine and dihalide). The polymer was precipitated by pouring the reaction mixture into a large excess amount of acetone

Table 1
Polymers for the production of polyelectrolyte sorbents (without counterions)

Polymer	Structural formula	Colour
3-X		White
6-X		White
Ph-X		Light cyan[a]
Dp-X		Bright yellow
2HP-8		White

[a] The colour appears to be due to impurities resulting from the diamine oxidation.

and dried under $CaCl_2$ at 25°C for a week. Yields of the ionenes were nearly 50%. Thus, the following polymers were synthesised and used for the preparation of the sorbents: aliphatic ionene with hydroxyl groups (2HP-8 ionene); mixed aliphatic–aromatic ionenes (3-X and 6-X ionenes); aromatic ionene (Ph-X ionene); and viologen (Dp-X ionene). All other aliphatic ionenes mentioned in the article were prepared earlier as described [3].

2.3. Synthesis of anion exchangers

The synthesis of ion exchangers involves a modification of the matrix by addition of suitable cation exchanger to the solution of water-soluble polymer. Electrostatic interactions result in formation of stable polyelectrolyte complex, the surface becomes positively charged (due to extra non-compensated charges of nitrogen atoms in the polymer chain). Modification of matrices was carried out as follows. A weighed portion of silica (or other matrix) was placed in a beaker and moisturised with a small quantity of water, then 10 ml of deionised water was added. The mixture was stirred for 30 min under 70–80°C. Then 1.3 mM of polymer-modifier was added. The solution was mixed for an extra 20 min, then it was used for packing columns under a pressure of 150–200 bar.

3. Results and discussion

3.1. Selection of optimal cation-exchange capacity

Pellicular packing materials for ion chromatography are commonly formed using permanent

electrostatic interactions, and have to fulfil certain requirements to be robust and useful [17]. One of these requirements is low capacity of produced anion exchangers.

Such an approach to the synthesis of polyelectrolyte sorbents implies an explicit dependence of the capacity and other properties of the synthesised anion exchanger on the capacity of the cation exchanger used as a matrix. If the capacity of the cation exchanger is too low, polymer molecules would not be retained at the surface strongly enough, and the polyelectrolyte complex would decompose. This would result in a decrease in the capacity and degrade the working parameters of the column. On the other hand, if the capacity of the cation exchanger is too high, all the charged nitrogen atoms in the molecules of the modifier polymer would be used for forming bonds with sulfonic groups at the matrix surface. In this case, anion-exchange capacity would also be negligible. Thus, in order to find an optimum cation-exchange capacity suitable for synthesising polyelectrolyte anion exchangers, we selected three appropriate sulfonated materials, which differed in their capacity for sulfonic groups: Kank-CSt ($Q = 0.02$–0.03 mmol/g), Silasorb-S ($Q = 0.2$–0.3 mmol/g), and AG 50W-X2 ($Q = 0.9$–1.0 mmol/g). On the basis of these matrices, we synthesised polyelectrolyte anion exchangers and constructed sorption isotherms for modifier polymers. In all the cases, we used 4,6-ionene as a modifier, which was previously shown to have good characteristics [3] as a modifier (Fig. 1). For each cation exchanging matrix, we made chromatograms of inorganic ions. Satisfactory results were obtained only in the case of Silasorb-S. The average capacity for Silasorb-S-based sorbents is 0.08 mmol/g. Anion-exchange capacity in all other cases was negligible (retention time even for strongly retained components of the mixture is equal to the dead time). The sorbents based on Silasorb-S are characterised by a constant capacity at least of 2 months, provided an eluent without ionene admixtures is used. The analysis of the dependences and chromatograms of inorganic ions for various matrices allows us to reach the following conclusion. The optimum values of sorbent capacity showing good anion-exchange properties are in the range of 0.2–0.5 mmol/g. In the case of lower cation-exchange capacities (at the level of 0.01 mmol/g) the

modifier polymer is not retained on the matrix surface. In the case of a higher capacity (at the level of 1 mmol/g), all of the positively charged nitrogen atoms in the polymer molecules turn out to be blocked with sulfonic groups at the matrix surface.

It is known [3] that preparation of polyelectrolyte sorbents under an increased temperature results in a twofold increase in the efficiency and capacity of the prepared sorbent compared to the synthesis under room temperature. Thus, for Silasorb-S sorbent, we studied two dependences, for room and an increased temperature (Fig. 2). An increase in the temperature of the synthesis of polyelectrolyte sorbents results in an increase in the amount of sorbed polymer-modifier. The cause appears to lie in a change in the conformational structure of polymer molecules: they unfold and, thus, are fixed at the matrix. Under cooling, steric hindrances prevent a change in the configuration, and a larger number of anion exchanging centres become accessible.

3.2. Ion chromatographic behaviour of common inorganic anions

To study ion chromatographic behaviour of ions on prepared polyelectrolyte sorbents, we selected the single-column variant of ion chromatography with potassium hydrogenphthalate as an eluent. Phthalate has a strong affinity to the separating sorbent; thus, rapid and selective separation of anions is obtained for low concentrations of the eluting ion. Using a phthalate eluent with pH 6.9–7.0, simultaneous determination not only of ions like Cl^-, NO_3^-, SO_4^{2-} but also of strongly retained species like thiocyanate or perchlorate, which are not removed from the column with an eluent with a lower pH, is possible. A typical chromatogram of inorganic ions on polyelectrolyte sorbents modified with aromatic ionenes is shown in Fig. 3. Scales of relative retention of inorganic anions on polyelectrolyte sorbents are presented in Fig. 4. It seemed interesting to compare the selectivity of prepared polyelectrolyte sorbents with aromatic ionenes as modifiers with similar ion exchanging materials based on aliphatic ionenes. Somewhat surprising was that retention of sulfate on synthesised sorbents is higher than in the case of aliphatic analogues. In other words, aromatic modifiers act as aliphatic ionenes with a lower chain and a
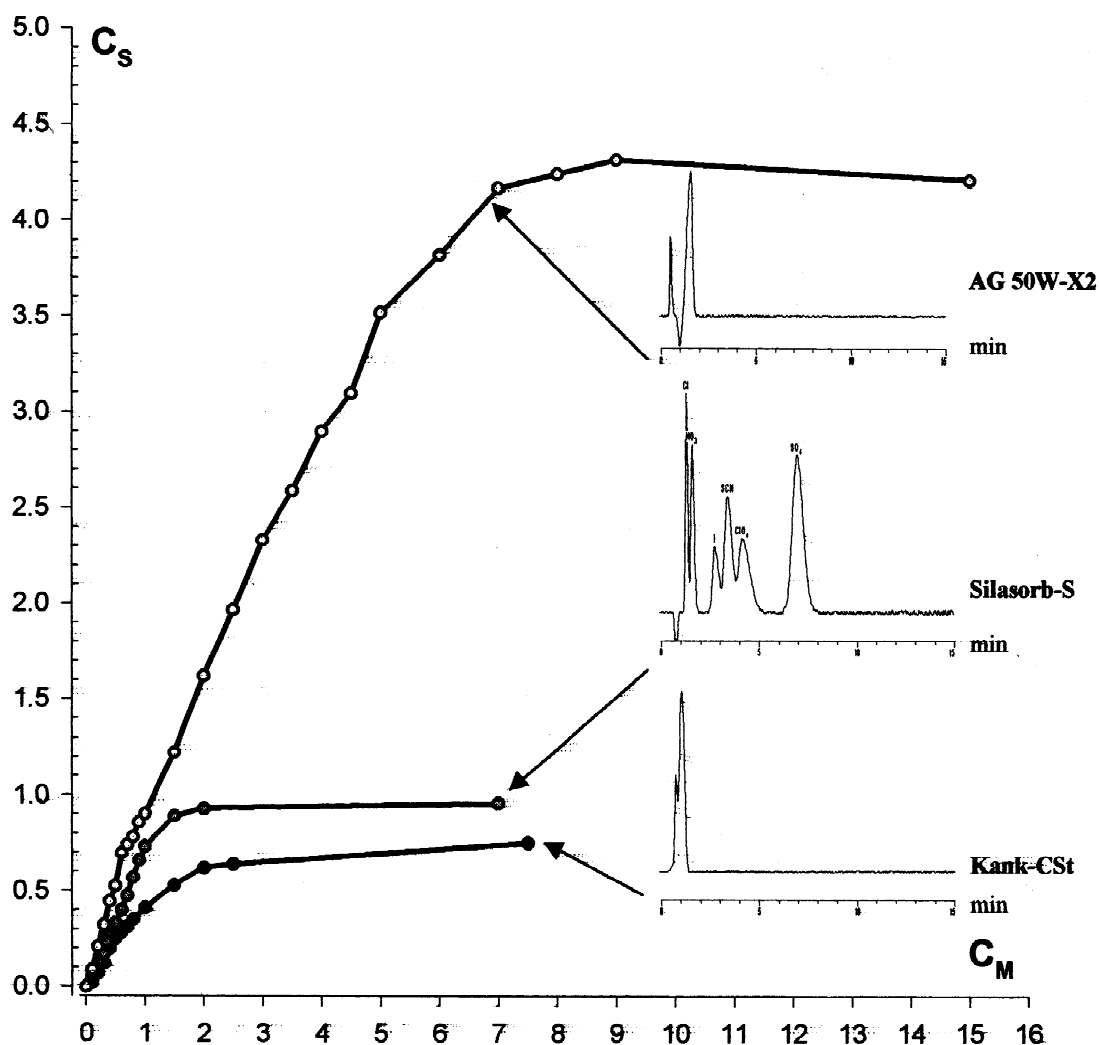
Fig. 1. Isotherms of sorption of 4,6-ionene at room temperature on some matrices with different cation-exchange capacities: Kank-CSt ($Q=0.02$–0.06 mmol/g); Silasorb-S ($Q=0.2$–0.3 mmol/g); AG 50W-X2 ($Q=0.9$–1.0 mmol/g), and observed chromatograms of inorganic anions.

high charge density. For instance, selectivity of 3-X ionene to inorganic anions is closer to that of 2,8-ionene than to 3,8-ionene. This effect is possibly due to the fact the molecule of the aromatic ionene is more rigid. The benzene ring does not allow the polymer chain to fold in globules. A similar structure is characteristic for short-chain aliphatic ionenes. As a result, aromatic ionenes show "more hydrophilic" properties than their aliphatic analogues.

It may be concluded that the selectivity of poly-electrolyte sorbents is primarily affected by the conformational structure of the modifier ionene, and only secondarily by the number of carbon atoms between nitrogen atoms in the chain. This is confirmed by the positions of aromatic ionenes on the similarity diagram. The procedure for constructing such a diagram has been described previously in detail [3]. Briefly, at the first stage the starting data were pairwise ratios of retention times (selectivity factors) of chloride, sulfate, thiocyanate and per-chlorate. These parameters were used in cluster analysis to outline similar groups (clusters). The
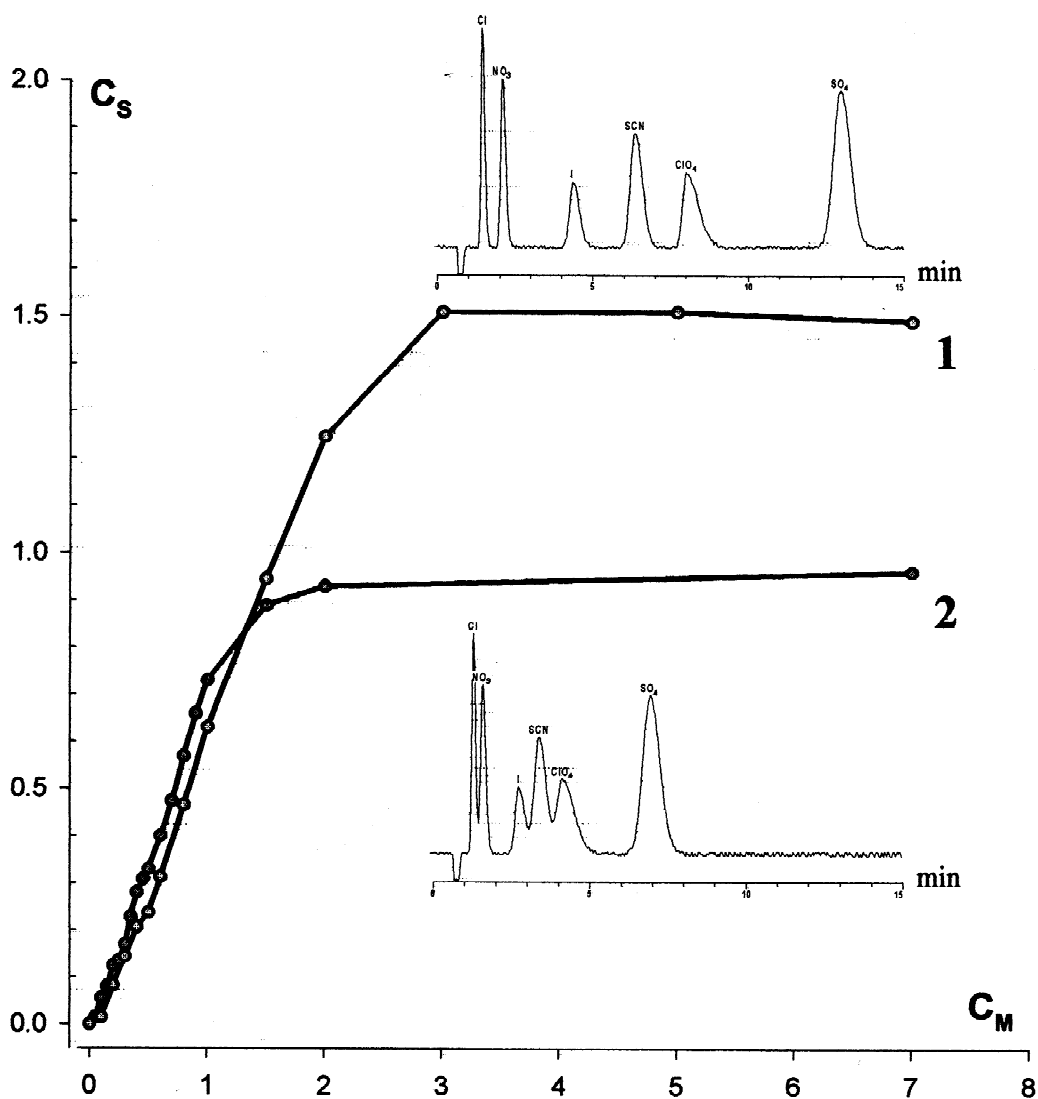
Fig. 2. Isotherms of sorption of 4,6-ionene at different temperatures on Silasorb-S and observed chromatograms of inorganic anions, (1) at 70°C, (2) at 20°C.

calculated picture looks like a genealogical tree (Fig. 5). The ionenes form pairs with more or less similar properties.

Fig. 5 shows that from the viewpoint of ion chromatography, 3-X and 2HP-8 ionenes are virtually identical and drop into the group of ''intermediate'' modifiers, in spite of the fact, that 2HP-8 ionene is a priori more hydrophilic due to presence of hydroxyl groups in the molecule. 6-X, Ph-X, Dp-X ionenes, which are also in this group, are not shown for clarity. It should be noted once again that, as Fig. 5 shows, 3-X ionene, by the similarity of its chromatographic properties, is closer to short-chain aliphatic analogues (2,8- and 4,6-ionenes) than, e.g., to 3,8-ionene, which has the same number of carbon atoms between nitrogen atoms.
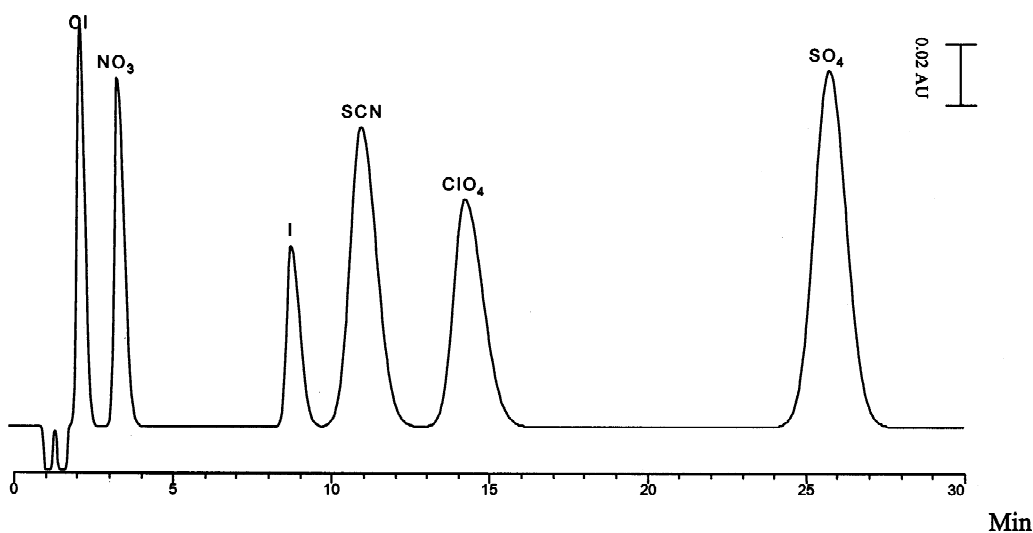
Fig. 3. The typical chromatogram of the mixture of anions on polyelectrolyte sorbents modified by aromatic ionenes. Sorbent: Silasorb-S. Modifier: 3-X ionene. Column: 50×3 mm. Indirect UV detection at 256 nm. Eluent: 0.3 mM potassium hydrogenphthalate, pH 6.9. Flow-rate: 1.0 ml/min.

3.3. Ion chromatographic behaviour of aromatic acids

Anomalous hydrophilic behaviour of ions on polyelectrolyte sorbents with aromatic ionene as modifiers is characteristic only for inorganic anions. The behaviour of anions of aromatic acids, 1-naphthalenesulfonic acid among them (Fig. 6), is different. The figure shows that the retention time of 1-naphthalenesulfonic acid in the case of a sorbent of
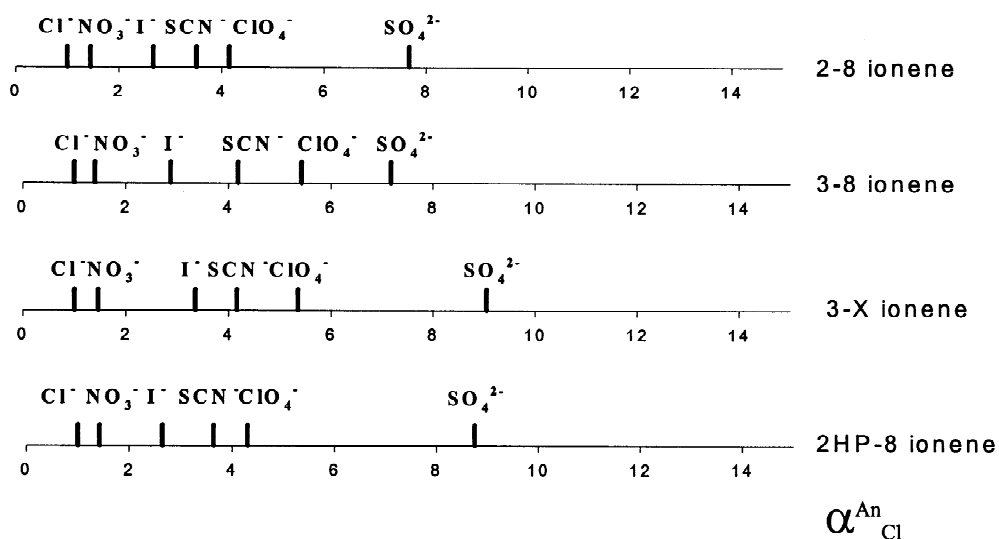

Fig. 4. The selectivity scales of the synthesised polyelectrolyte sorbents. Chromatographic conditions as in Fig. 3.
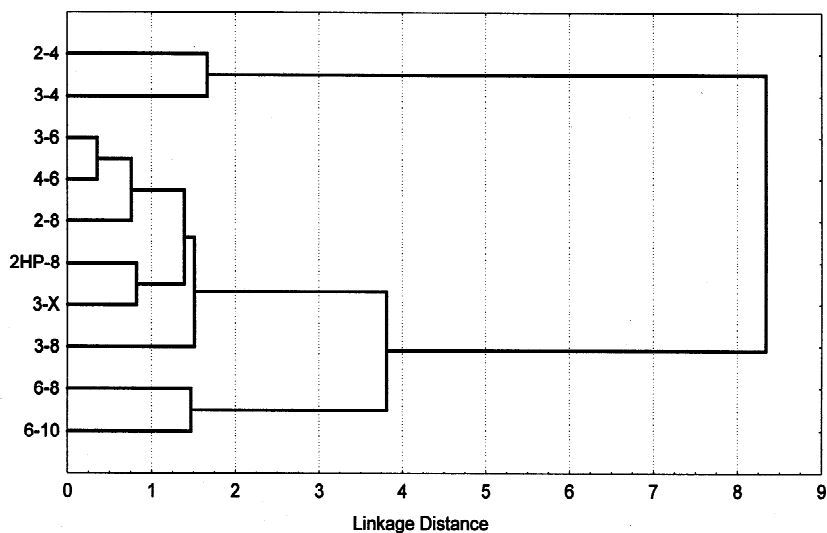
Fig. 5. Tree diagram of similarity of packing materials.

aromatic 3-X ionene is higher than for a sorbent modified with its aliphatic analogue, 3,8-ionene. This appears to be due to π–π interaction of aromatic systems of 3-X ionene and 1-naphthalenesulfonic acid. Analogously, the study of the behaviour of p-substituted (p-Cl-, p-Br-, p-I- and p-OH-) benzoic acids on synthesised polyelectrolyte sorbents resulted in higher selectivities than for aliphatic ionenes.
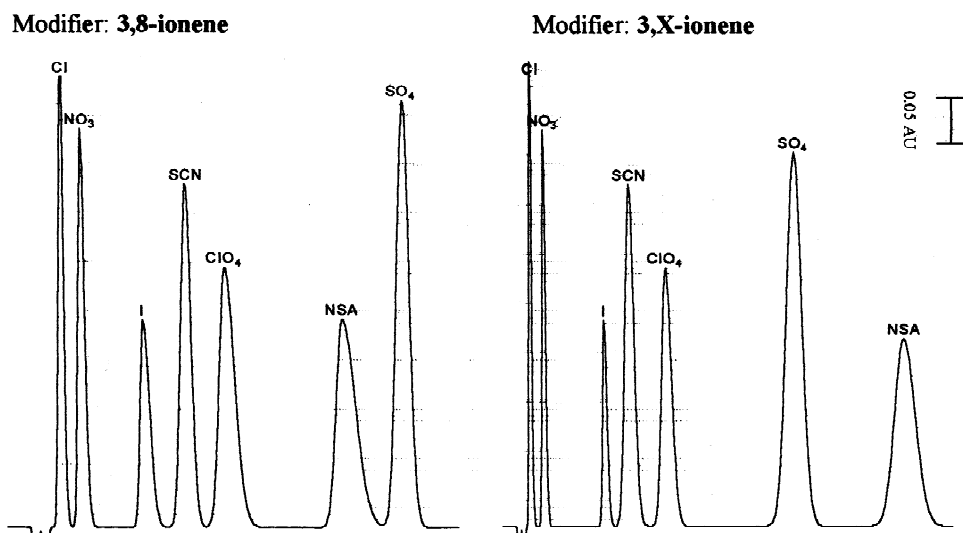

Fig. 6. The chromatograms of the mixture of anions and 1-naphthalenesulfonic acid. Chromatographic conditions as in Fig. 3.

4. Conclusions

We found that aromatic ionenes having a rigid structure of polymer chains, used as modifiers for synthesising polyelectrolyte sorbents and ion chromatographic determination of inorganic anions, are similar to their aliphatic analogues with shorter chains with a high charge density. The determination of aromatic acids with polyelectrolyte sorbents based on aromatic ionenes is more selective than with the use of their aliphatic analogues due to specific $\pi–\pi$ interactions.

Acknowledgements

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