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Polyelectrolyte sorbents based on aliphatic ionenes for ion chromatography

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Abstract

2-4, 3-4, 2-8, 3-8, 3-6, 4-6, 6-8, 6-10-ionenes (polymers with quaternary nitrogen atoms in the main chain) served as modifiers in synthesizing polyelectrolyte sorbents for ion chromatography. The approaches to the synthesis and their stability are discussed. Cluster analysis was applied to separate aliphatic ionenes to three groups as chromatographic modifiers, namely hydrophilic, hydrophobic, and intermediate. Each group is characterized by a certain selectivity to sulfate, perchlorate, iodide and thiocyanate. The sorbents show high selectivity and efficiency up to 15 000 theoretical plates per meter.   © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ionenes are polymers with a quaternary nitrogen atoms in the main chain. The range of substances that fulfill this definition is wide. In this study, we consider polyammonium salts, which are most commonly called ionenes. The term 'ionenes' was introduced by Rembaum et al. in 1968 [1]. Within the last years more than 200 papers and patents devoted to the synthesis and properties of new ionenes have been published.

There are several different approaches to name ionenes depending on the composition of functional groups between quaternary nitrogen atoms. The

common formula of an ionene can be expressed as $-[R_2N^+-(CH_2)_n-NR_2^+-(CH_2)_m]-_x$. Almost all the ionenes are produced by a polycondensation reaction from two monomers; thus, their names are composed from two parts determined by the monomers. For instance, aliphatic ionenes are denoted with two digits separated with a comma, a hyphen, in brackets, and in parentheses (or even without them) like n-m ionene, where n and m is the number of CH_2 groups between the nitrogen atoms. It is assumed that n is the aliphatic part of a diamine and m is from a dibromide (or diiodide). Nevertheless, many authors do not use this non-strict rule and indicate the smaller part first (like 3-6 ionene). The first example of ionene based ion chromatographic sorbent was demonstrated using 2-5 ionene [2].

This study was the first experience in using aliphatic ionenes as modifiers for producing sorbents

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for ion chromatography. Also, the aim of the work was to study the effect of the structure of an ionene on ion chromatographic selectivity of inorganic anions.

2. Experimental

2.1. Instrumentation and chemicals

The experiments were carried out with IC-1000 chromatographs (Eppendorf-Netheler Hinz, Division Biotronik, Germany). Uvidec-1000-IV spectrophotometric detectors (Jasco, Japan) with tuneable wavelength was used throughout. Indirect UV detection at 254 nm was used. Stainless-steel columns (50×3 mm) were used throughout. Injected sample volume was 50 µl. Flow rate was 1 ml/min. For the separation of strongly retained anions, a 0.3 mM solution of potassium hydrogenphthalate was used, eluent I (pH 6.9±0.1). To separate weakly retained ions, a 2.0 mM solution of benzoic acid was used, eluent II (pH 5.5±0.1). The following matrices for the synthesis of the packing materials were used:

1. Silasorb C_{18} (10 µm), reversed-phase silicas, the total surface 300–600 m^2/g, diameter of pores 7–10 nm (Lachema, Brno, Czech Republic);
2. Silasorb S (5 µm), reversed-phase silicas with chemically-bonded sulfo groups (Lachema);
3. Diasorb C_{16}, and Diasorb-Ph (10 µm), reversed-phase silicas with aliphatic or phenyl groups, respectively, on the surface. (BioChimMak, Moscow, Russia);
4. Silasorb 600 (10 µm) normal-phase silica, total surface 600 m^2/g, (Lachema);
5. Spheron 100 (<25 µm), copolymer of oxyethyl methacrylate and ethyl methacrylate (Lachema).
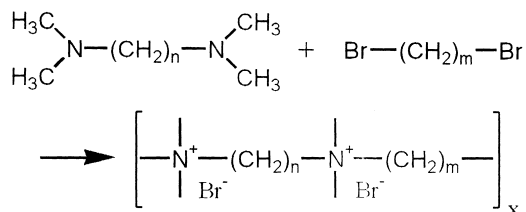
Deionized water was obtained from a Barnstead Fstreem III water purification system (UK). It was used for preparing all the solutions.

N,N,N',N'-Tetramethyl-1,3-diaminopropane, $N,N,$-N',N'-tetramethyl-1,6-hexanediamine, 1,4-dibromobutane, 1,8-dibromooctane, 1,10-diiodododecane were obtained from Aldrich (USA). N,N,N',N'-tetramethylethylenediamine was obtained from ICN (USA). 3,6-Ionene was obtained from Sigma and used 'as is'. Solvents [acetone, dimethylformamide (DMF)] were spectral grade and used without further purification.

2.2. Synthesis of ionenes

The most widespread method for synthesizing ionenes is a multiple Menshutkin reaction (N-alkylation):

$$\underset{H_3C}{\overset{H_3C}{\Large\diagdown}} N{-}(CH_2)_n{-}N \underset{CH_3}{\overset{CH_3}{\Large\diagup}} \quad + \quad Br{-}(CH_2)_m{-}Br$$

$$\longrightarrow \left[{-}\overset{|}{\underset{Br^-}{N^+}}{-}(CH_2)_n{-}\overset{|}{\underset{Br^-}{N^+}}{-}(CH_2)_m{-} \right]_x$$

We used this reaction for synthesizing ionenes. The following description illustrates the method used in the synthesis of 2-4, 3-4, 2-8, 3-8, 4-6, 6-8, and 6-10 ionenes. The polymerization 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 24 h. The polymer was precipitated by pouring the reaction mixture into a large excess amount of acetone and dried under vacuum at 25°C for a week. Polymers obtained were hygroscopic white powders. Yields of the ionenes were nearly 50%. Calculated molecular masses of the polymers were from 8000 to 14 000.

3. Results and discussion

3.1. Matrix selection and sorbent synthesis

Polyelectrolyte sorbents are synthesized by modifying a suitable matrix with solutions of cationic polyelectrolytes [2,3]. Certainly, matrices should have relatively high affinity to polymers (for strong sorption) and stability to eluents used and be commercially available. Synthesis of polyelectrolyte sorbents implies at least two approaches. The first way is based on treatment of a suitable matrix with a solution of an anionic surfactant or an appropriate dye, which produces a layer of negatively charged sulfo groups at the surface. Next, such an intermediate material is modified with a polymer solu-

tion. Electrostatic interactions result in formation of stable polyelectrolyte complex, the surface becomes charged positively (due to extra non-compensated charges of nitrogen atoms in the polymer chain). Another approach is to select a matrix with chemically grafted sulfo groups and to modify it with a polymer solution. In this case, no intermediate treatment with an anionic surfactant is required. Moreover, estimated stability of such materials seems to be higher than in the previous case. We studied both approaches.

The matrices were modified as follows: a weighed portion was placed into a beaker and moisturised with a small quantity of water; then 10 ml of a 0.1 mM solution of the intermediate modifier was added. The mixture was stirred for 30–60 min under room conditions. The produced cation exchanger was separated from the excess of modifier by decantation and a certain amount of a dry ionene was added. The solution was mixed under room or an increased temperature for an extra 20 min, then it was used for packing columns under a pressure of 200 bar. The average efficiencies were calculated from chromatograms of a test mixture of anions (Cl^-, NO_3^-, I^-, SCN^-, SO_4^{2-}, ClO_4^- with concentrations of 0.1 mM of each component). The results are shown in Table 1. Thus, we shown that a solution of DBSA (dodecylbenzenesulfonic acid) cannot be used as an intermediate modifier for Spheron 100. DBSA is readily

washed from the surface of Spheron 100, and the layer of sulfo groups necessary for binding the polymer is not formed. Spheron 100 can be modified with a dye containing sulfo groups (we used Congo Red). In this case, the dye is retained at the surface due to very strong absorption. However, the efficiency and stability of sorbents of this type proved too low. The most promising results were obtained for Silasorb C_{18}-DBSA and Silasorb S matrices. Working with Silasorb C_{18}-DBSA-Ionene results in a decrease in the efficiency and retention times with time, this accounts for the washing down of DBSA [3].

We observed an interesting effect of a sharp increase in the efficiency and capacity of the sorbent when the synthesis is performed at an increased temperature (Fig. 1). It can be accounted for the fact that ionenes, especially those with long aliphatic chains, are flexible enough to give various conformation structures. On a change in the temperature, the conformation of polymer molecules changes and they are 'fixed' at the layer of sulfo groups of the matrix. It is possible that heating somewhat unbends ionene molecules and they sorbed at the surface more strongly and uniformly and give a larger amount of quaternary nitrogen atoms available for ion exchange. After the synthesis, cooling, and performing the analysis under room conditions do not change this conformation. Thus, properties of

Table 1
The comparison of efficiency of polyelectrolyte sorbents produced by different methods of synthesis (DBSA=dodecylbenzenesulfonic acid, DNDSA=dinonylnaphtoldisulfonic acid). Column 50×3 mm, Eluent 1, flow rate 1 ml/min

Initial matrix	Intermediate modifier	Mass ratio matrix/3-6 ionene	Average efficiency (theoretical plates per meter)
Silasorb 600 (10 μm)	DBSA	4.0	No peaks[a]
Spheron 100 (<25 μm)	No	3.2	No peaks[a]
Spheron 100 (<25 μm)	DBSA	5.3	No peaks[a]
Spheron 100 (<25 μm)	Congo Red	2.3	1800
Silasorb C_{18} (10 μm)	DBSA	2.8	5200
Silasorb C_{18} (10 μm)	DBSA	1.2	4900
Silasorb C_{18} (10 μm)	DNDSA	3.5	1500
Diasorb C_{16} (10 μm)	DBSA	3.7	2000
Diasorb Ph (10 μm)	DBSA	5.7	2200
Silasorb C_{18} (7.5 μm)	DBSA	1.0	5300
Silasorb S (5 μm)	No	2.1	4000
Silasorb S (5 μm)	No	1.0	5800
Silasorb S (5 μm)[b]	No	1.0	15 100

[a] Anion-exchange capacity is too low.
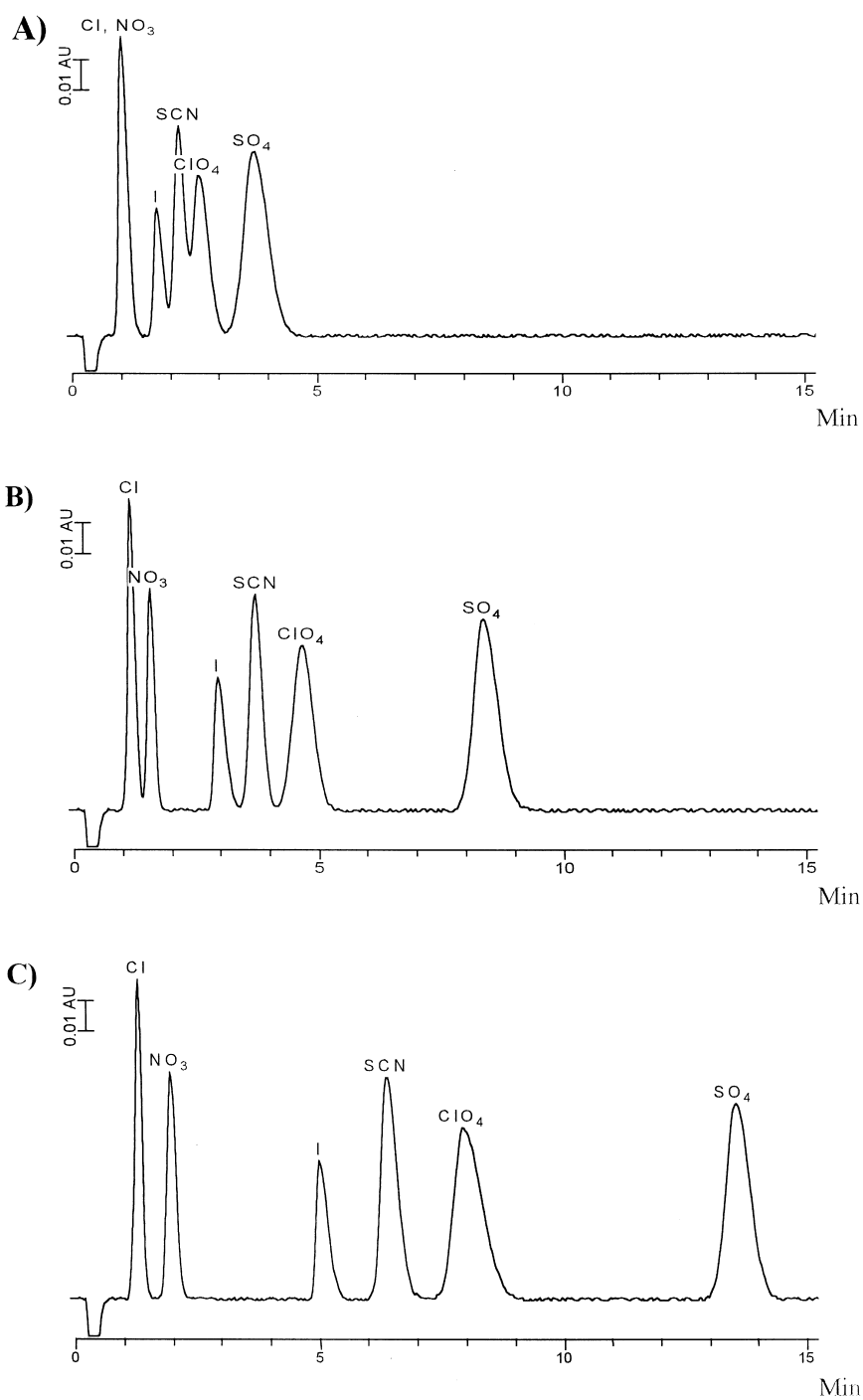
[b] Sorbent was synthesized at 80°C.

Fig. 1. The chromatograms of the mixture of anions vs. temperature of synthesis. Sorbent: Silasorb S modified by 3-6 Ionene; Column: 50×3 mm. Detector: UV: 254 nm. Eluent: 0.3 mM potassium hydrogenphthalate, pH 6.8, flow rate 1.0 ml/min. (A) 25°C, (B) 45°C, (C) 80°C.

synthesized sorbents are different. The stability also increases. For instance, a Silasorb S-ionene sorbent synthesized at 80°C did not show any change in the efficiency and selectivity during three months of use.

It is known that physicochemical properties of the solvent used at the stage of column packing usually affect the efficiency. We found that water, 1 M NaCl, a mixture of isopropanol–water (1:1), a 50% solution of glycerol nearly not affect the quality of the prepared polyelectrolyte sorbent and the image of obtained chromatograms.

Thus, the most advantageous approach to produce polyelectrolyte sorbents on the basis of aliphatic ionenes for studying their selectivity is modification

of Silasorb S with an ionene at 80°C. The mass of dry ionene was selected so that the total number of quaternary nitrogen atoms per 1 g of the sorbent was the same as in 3-6 ionene, provided the ratio of masses of the ionene and matrix was 1:1. (A further increase in the amount of the ionene gives neither an increase in the capacity nor an increase in the efficiency of the sorbent). All the subsequent studies were based upon this approach.

3.2. Stability of synthesized sorbents

The stability of synthesized sorbents depends on matrix, intermediate modifier, and eluent composi-
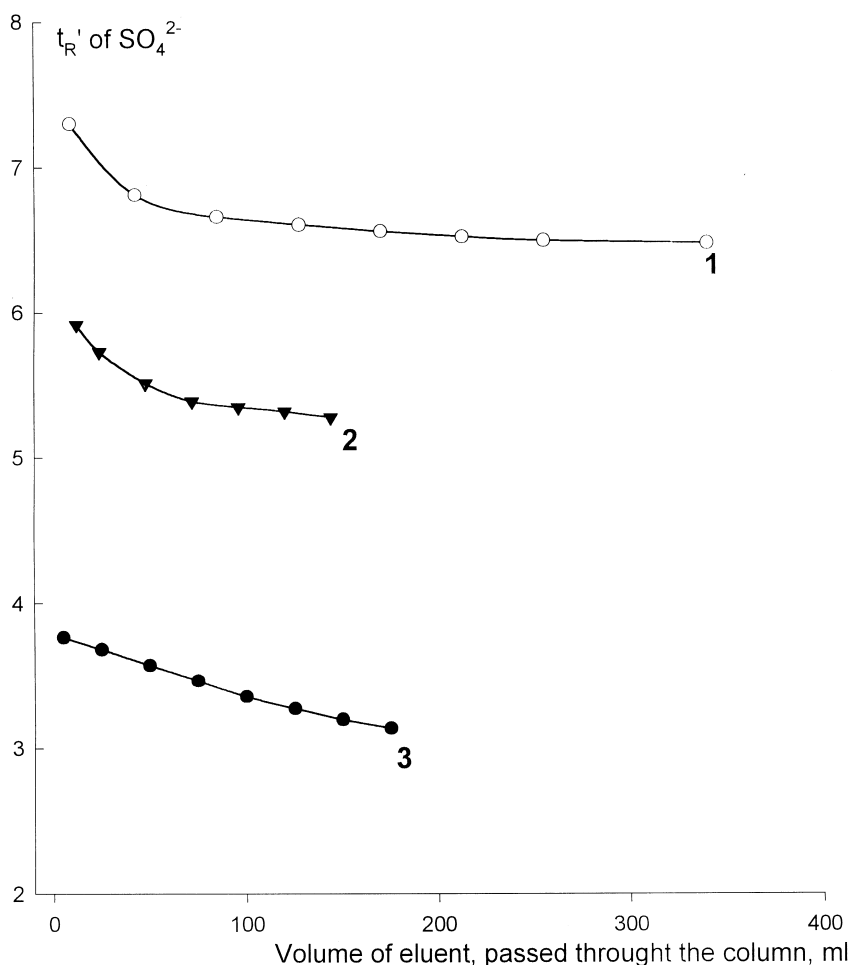

Fig. 2. The stability of synthesized sorbents. Eluent: 0.3 mM potassium hydrogenphthalate, pH 6.9, flow rate 1 ml/min, column 50×3 mm. (1) Silasorb S-3-6 Ionene (synthesized under 45°C); (2) Silasorb C18-DBSA-3-6 Ionene; (3) Spherone 100-Congo Red-3-6 Ionene.

tion. Sorbents synthesized using a Silasorb C_{18} matrix with an intermediate modifier are less stable than sorbents prepared using Silasorb S (Fig. 2). A sorbent synthesized using a Spheron 100 with organic dyes as intermediate modifiers is unstable and rapidly loses capacity (Fig. 2 line 3). Silasorb S proved to be the most suitable among studied matrices. The sorbents on its base are characterized by a constant capacity at least for two months, provided an eluent without ionene admixtures is used. The total ion-exchange capacity of sorbents

based on Silasorb C_{18}-DBSA proved to be 0.06 mM/g as an average; the average capacity for Silasorb-S based sorbents is 0.08 mM/g.

3.3. Selectivity of polyelectrolyte sorbents

Polyelectrolyte sorbents on the basis of aliphatic ionenes show good selectivity for separating inorganic anions (Fig. 3). To compare synthesized sorbents, we produced chromatograms of test mixtures under similar chromatographic conditions. To
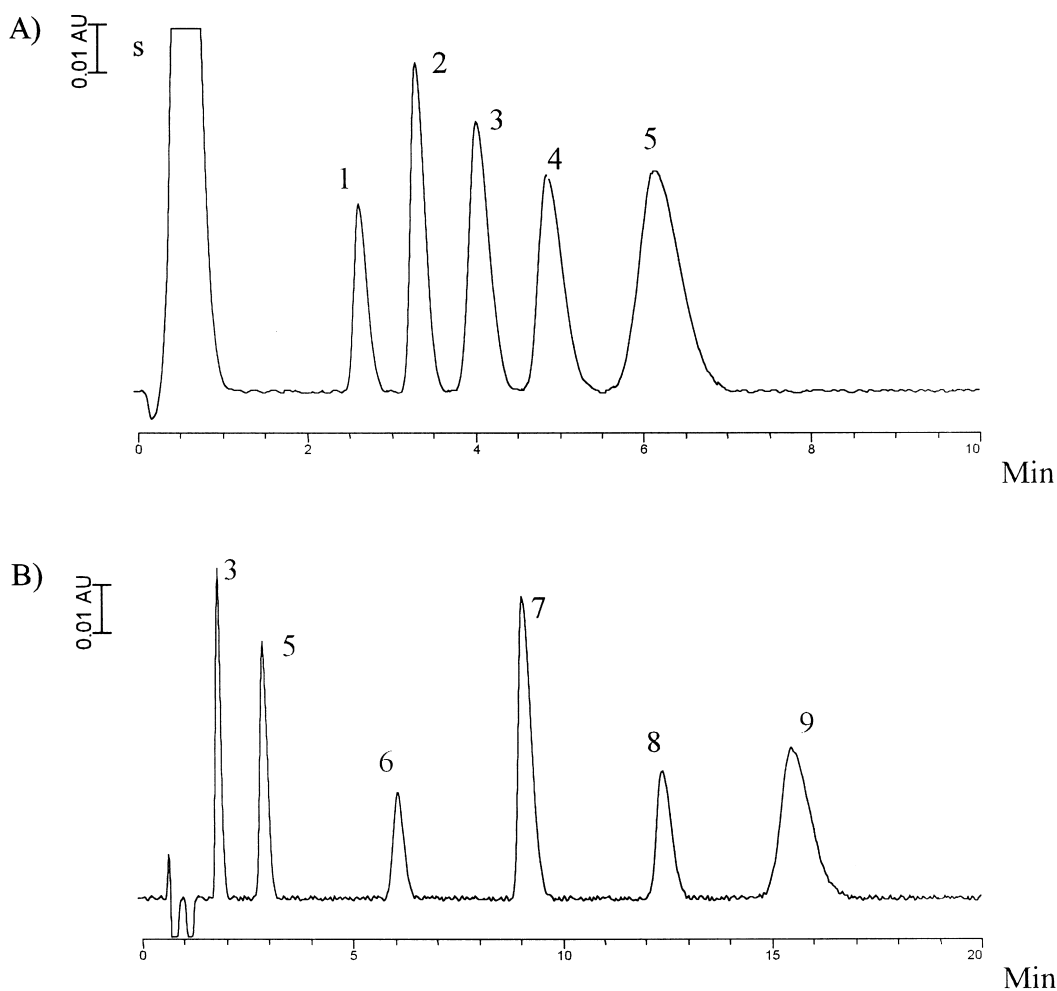

Fig. 3. The chromatograms of the mixtures of weakly and strongly retained anions. (A) Sorbent: Silasorb S modified by 4-6 ionene (synthesized under 75°C). Eluent II: pH 7.0, other conditions as in Fig. 1; (B) Sorbent: Silasorb S modified by 6-10 Ionene (synthesized under 75°C). Eluent I: pH 5.5, other conditions as in Fig 1. Peaks: 1=iodate, 2=formate, 3=chloride, 4=nitrite, 5=nitrate, 6=iodide, 7=sulfate, 8=thiocyanate, 9=perchlorate.

separate a mixture of chloride, nitrate, iodide, thiocyanate, sulfate, and perchlorate, we used eluent I. To separate iodate, acetate, formate, bromate, chloride, nitrite, bromide, and nitrate, we used eluent II. Selectivity scales are presented in Figs. 4 and 5. One can see that the selectivity of sorbents to sulfate, perchlorate, and thiocyanate is drastically different. Is it possible to find out any regularities that can be used to describe sorbent properties and/or to predict

the properties of new sorbents without synthesizing them? To answer this question, we performed a cluster analysis of selectivity data for a series of Silasorb S-ionene sorbents.

At the first stage of cluster analysis, we determined variance weights of various parameters that can be used in a further classification (Table 2). The starting data were pairwise ratios of retention times (selectivity factors). Note that the maximum variance
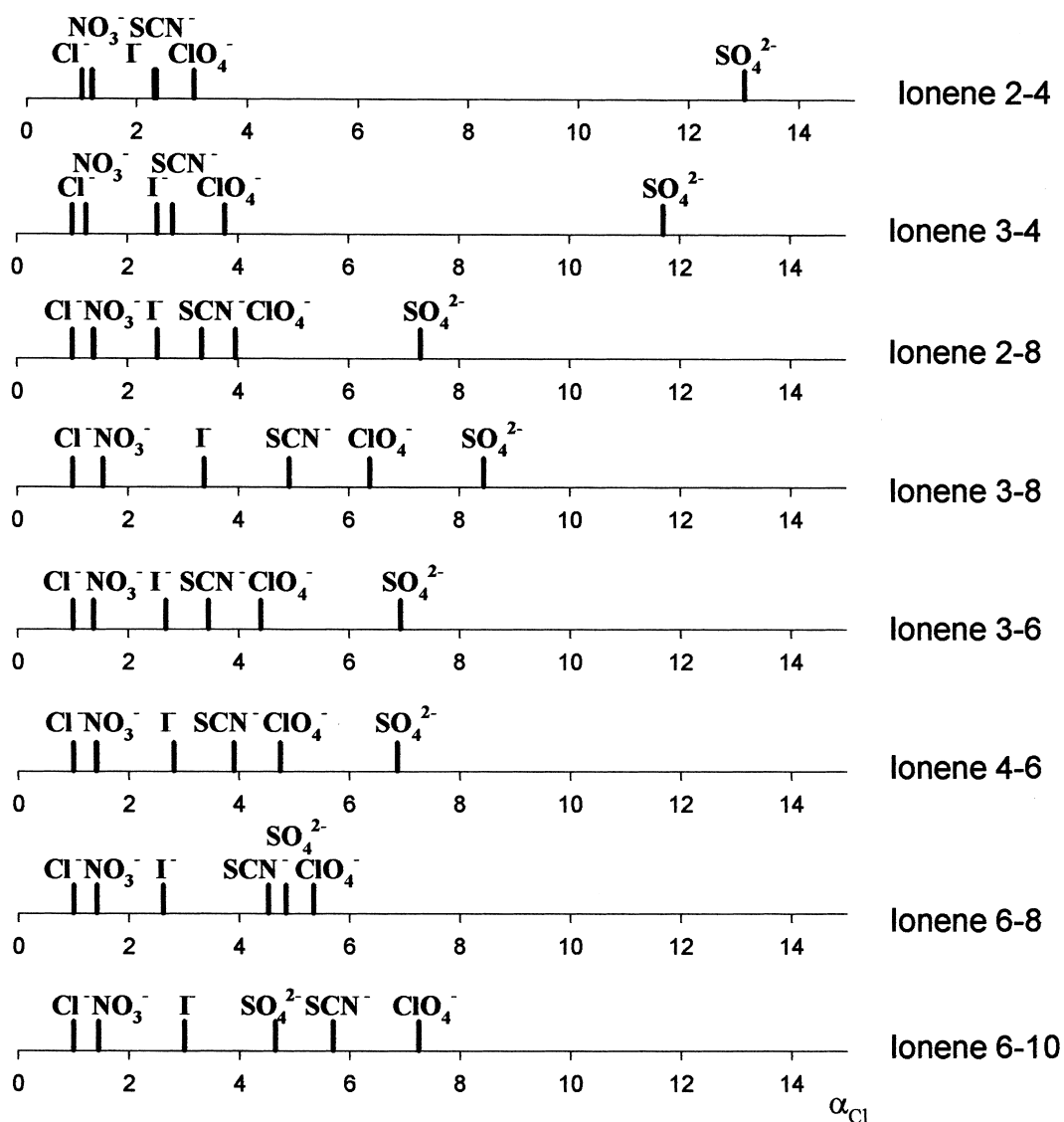

Fig. 4. The selectivity scales of the synthesized polyelectrolyte sorbents. Eluent II: pH 7.0, other conditions as in Fig 1.
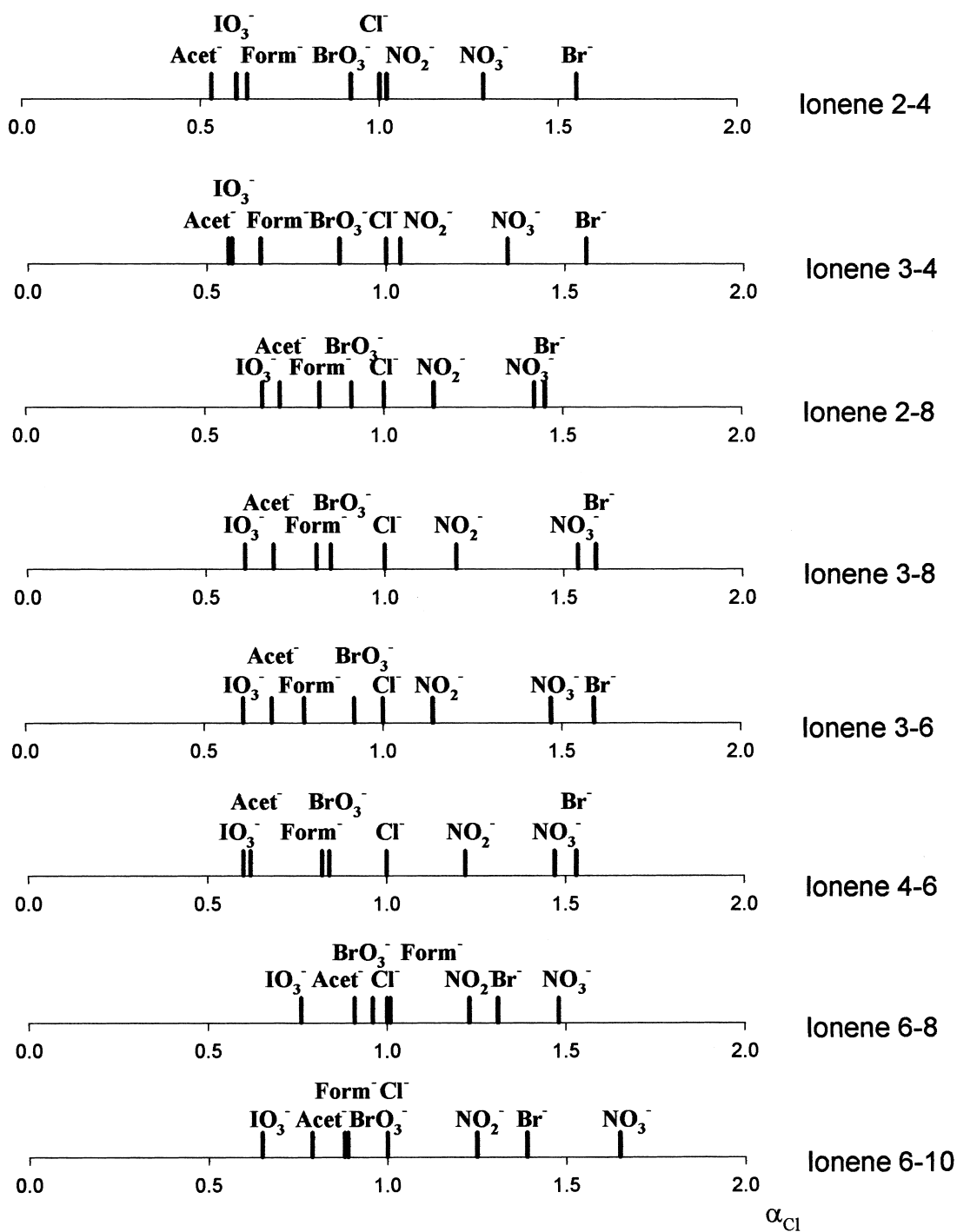
Fig. 5. The selectivity scales of the synthesized polyelectrolyte sorbents. Eluent I: pH 5.5, other conditions as in Fig 1.

Table 2
Dispertion weights of different parameters calculated for estimation of similarity of ionene-based packing materials

Parameter	Total dispertion weight	
	Absolute	in %
$\alpha(NO_3^-/Cl^-)$	6.4	7.6
$\alpha(I^-/Cl^-)$	3.8	4.8
$\alpha(SCN^-/Cl^-)$	6.0	7.2
$\alpha(SO_4^{2-}/Cl^-)$	13.7	17.0
$\alpha(ClO_4^-/Cl^-)$	5.0	5.9
$\alpha(ClO_4^-/SO_4^{2-})$	8.9	10.6
$\alpha(ClO_4^-/SCN^-)$	3.9	4.6
$\alpha(SO_4^{2-}/SCN^-)$	10.4	12.3
$\alpha(SO_4^{2-}/I^-)$	11.1	13.5
$\alpha(SCN^-/I^-)$	11.0	13.2
$\alpha(I^-/NO_3^-)$	2.8	3.3
Total sum	83	100

weights (and, therefore, classification ability) are observed for sulfate–iodide, sulfate–perclorate, sulfate–thiocyanate, thiocyanate–iodide, and sulfate–chloride selectivities. These properties provide the

total of 80% of the total variance. Thus, with a fair degree of confidence, one can assume that in order to characterize chromatographic properties of a polyelectrolyte sorbent on the basis of an aliphatic ionene, it is sufficient to produce a chromatogram of iodide, thiocyanate, and perchlorate and compare their pairwise selectivities. Selected parameters were used in cluster analysis. Obtained histograms of 'ionene vs. similarity of the sorbents' show that all of the sorbents drop into three groups (Figs. 6 and 7).

The first group is comprised by two sorbents on the basis of the most 'hydrophilic' sorbents, 2-4 and 3-4 ionenes. Theses polymers are characterized by two short (less than five carbon atoms) aliphatic chain fragments. The use of eluent I for these sorbents results in very long retention time for sulfate relative to other anions and a relatively low selectivity to hydrophobic anions (iodide, thiocyanate, and perchlorate) (Fig. 7a). If eluent II is used with these sorbents, acetate, formate, and iodate are
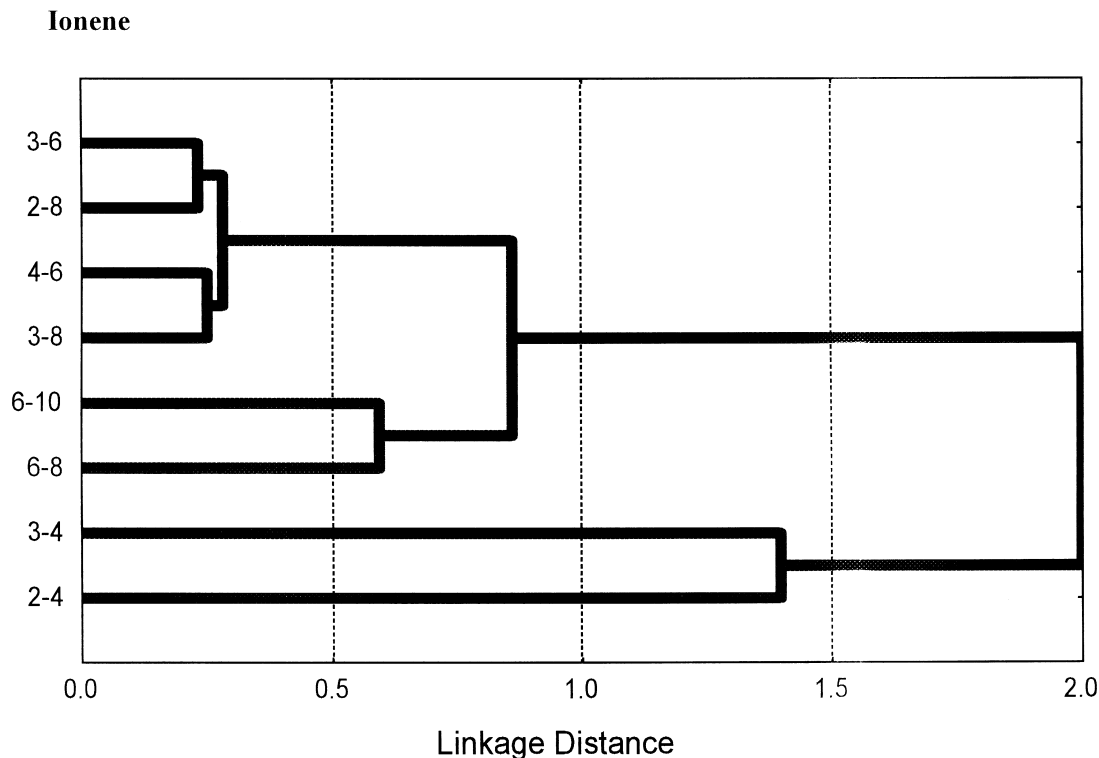
Ionene

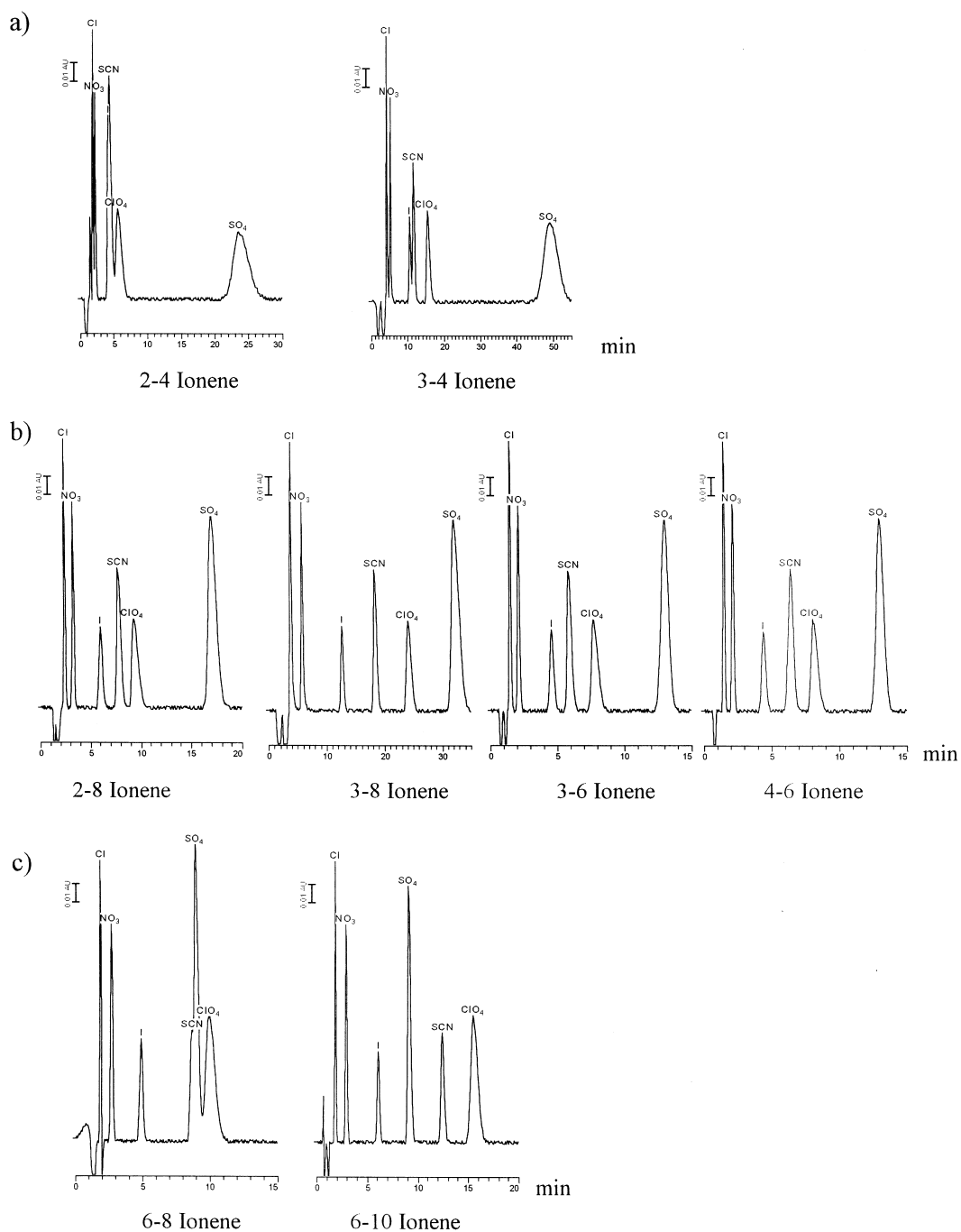Fig. 6. Tree diagram of similarity of packing materials. Single linkage. Eucledian distance.

Fig. 7. Typical chromatograms of inorganic anions for different groups of polyelectrolyte sorbents. Conditions as in Fig. 1.

eluted almost simultaneously; another group of similarly eluted anions consists of chloride, nitrate, nitrite, and bromide. In the latter group bromide is retained stronger than nitrate.

The next, so-called 'intermediate' group consists of sorbents on the basis of ionenes that has an aliphatic chain fragment with less than five carbon atoms, while the other fragment has more than five atoms. Eluent I does not affect the retention in the row SCN^-, ClO_4^-, SO_4^{2-} yet; however, the selectivity of determination of hydrophobic anions is much higher compared to the first group of sorbents (Fig. 7b). In the case of eluent II, the selectivity of separation of IO_3^-–acetate$^-$, BrO_3^-–formate$^-$, NO_3^-–Br$^-$ is not high enough. Under these conditions, the peaks of nitrate and bromide are fully overlapped; the peaks from chloride and nitrite are baseline-resolved.

Finally, the last group includes sorbents on the basis of 6-8 and 6-10 ionenes. These polymers are characterized by the length of both aliphatic chain fragments more than five methylene groups. Owing to a higher 'hydrophobicity' of such ionenes, the use of eluent I results in a considerably stronger retention of iodide, thiocyanate, and perchlorate. Contrary to this, sulfate, which is retained primarily due to electrostatic interactions, is eluted before thiocyanate and perchlorate (Fig. 7c). In the case of eluent II, the peaks from nitrite and bromide are overlapped. Thus, the retention of bromide continuously diminishes from group to group, and it is minimal for the last group.

It is interesting that such classification is in a good concordance with the structure of ionenes. For instance, the authors of [4] showed that ionenes with the number of methylene groups between two nitrogen atoms less than six has a rigid fibrillar structure. The case of 8-8 ionene is characterized by both fibrilar and globular structures. In the case of 6-10 ionene, the globular structure is prevailing, and this structure is the only found for 10-10 ionene. This proves that there is a certain critical distance between two nitrogen atoms, above which the phase composition of the polymer changes. Probably, a similar factor is responsible for changes in chromatographic properties of polyelectrolyte sorbents based on aliphatic ionenes.

Acknowledgements

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