Application of neutral hydrophobic hypercrosslinked polystyrene to the separation of inorganic anions by ion chromatography

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Abstract

Neutral hydrophobic hypercrosslinked polystyrene was shown to exhibit anion-exchange properties in the pH range 2.6–4.3 that can be attributed to the presence of protonated carbonyls in the framework of the polymer. This resin does not contain any other heteroatoms, except oxygen, responsible for the occurrence of positive charge at the surface. The anion-exchange selectivity of MN-200 and monosized spherical hypercrosslinked polystyrene to inorganic anions with diluted perchloric, nitric and sulfuric acid solutions as eluent was studied and the selectivity was found to be different from that observed for the common anion-exchangers. The main features of hypercrosslinked polystyrene are weak retention of sulphate and comparatively strong retention of nitrite that can be useful in practical ion chromatography. The influence of column temperature on the retention was investigated. Calculated adsorption heats are in the range from −2 to 19 kJ/mol. The retention mechanism of inorganic anions on neutral hypercrosslinked polystyrene includes both ion-exchange and hydrophobic interactions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, LC; Polystyrene stationary phases; Retention mechanisms; Heats of adsorption; Inorganic anions

1. Introduction

Polystyrene–divinylbenzene (PS–DVB) copolymer based anion exchangers present the most popular class of stationary phases in chromatography. A polymer matrix of these sorbents is hydrolytically stable in the broad pH range between 0 and 14 and it has a homogeneous surface without strong binding sites [1,2]. Generally, to obtain the required mechanical stability of the resin divinylbenzene is added to styrene during polymerization, so in the resulting material the two vinyl groups of DVB crosslink two polystyrene chains with each other (Fig. 1a). The percentage of DVB in the copolymer

is usually accepted as "crosslinking degree". The higher crosslinking degree results in the higher mechanical stability of the resin and also in its lower sensitivity to solvent changes causing swelling and shrinkage [1,2].

There is a different approach to the synthesis of polystyrene sorbents which have been proposed by Davankov and Tsyurupa [3]. It consists of making a large amount of rigid crosslinks between aromatic rings of linear polystyrene chains taken in the swollen state. Thus, the reaction of polystyrene or PS–DVB copolymers with monochlorodimethyl ether results in an extensive introduction of methylene bridges between aromatic rings of polystyrene (Fig. 1b). This reaction yields hypercrosslinked polystyrene (HC-PS) having a crosslinking degree of 100% and higher. In this case the term "crosslinking

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a)   b)
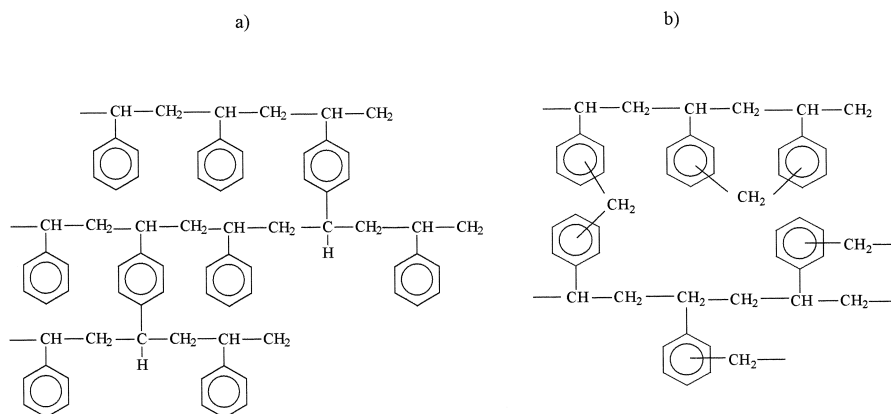

Fig. 1. The structure of polystyrene–divinylbenzene (a) and hypercrosslinked polystyrene (b) resins.

degree'' has another meaning it can be estimated as the ratio of double number of newly formed ($-CH_2-$) groups to the number of linked aromatic rings. HC-PS polymers have a highly developed inner surface (>1000 m^2/g) and display increased affinity to all kinds of organic solutes [3–5]. Also, in the swollen state, they are distinguished by an exceptionally rigid openwork structure of high permeability. In fact, the hypercrosslinked polystyrene represents a new generation of polystyrene networks, which follows the traditional gel-type and macroreticular copolymers and offers new possibilities for developing various adsorption materials.

Starting in the mid-1980s, HC-PSs have become frequently used in analytical practice, mainly, in solid-phase extraction of different organic compounds, such as phenols [4,6], long-chain aliphatic amines [7], synthetic dyes [4], lipids [4] and pesticides [8,9]. Now, a number of different HC-PC sorbents including neutral MN-200 are produced by Purolite [10], Merck, Supelco, IST and Spark Holland. Due to high rigidity and pressure resistance, microparticles of hypercrosslinked polystyrene can be considered as a promising stationary phase for HPLC. One of them, MN-200 (Purolite) has been successfully applied for separation of phenols [5,6], alkaline earth and transition metal ions [11–13], and polyaromatic hydrocarbons [5].

However, as it has been pointed out in many works [3–5], adsorption properties and retention mechanisms on MN-200 are not quite clear and are different from those for other types of polystyrene based polymer sorbents. Retention mechanism may involve not only hydrophobic, but also $\pi-\pi$ interactions. It is worthwhile underlining the increased affinity of hypercrosslinked polystyrene to aromatic molecules that can be attributed to the impact of $\pi-\pi$ interactions which in case of MN-200 is much higher than for other related sorbents [5]. Because of the highly developed microporous structure of hypercrosslinked polystyrene (Table 1), size exclusion may also affect the retention of substances.

One surprising property of neutral non-modified hypercrosslinked polystyrene is its wettability by water when one considers the hydrophobicity of this material. Recently, complete physical and chemical characterization of neutral hypercrosslinked polystyrene MN-200 was performed [8] and the presence

Table 1
Characteristics of porous structure of MN-200 obtained by different methods

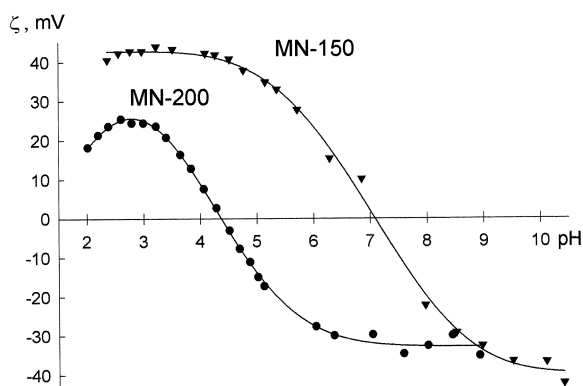| Characteristics	BET [10]	Inverse size-exclusion chromatography [5]
Mean diameter of micropores (nm)	1.5	1.1
Mean diameter of macropores (nm)	85–95	100
Surface area (m^2/g)	800–1000	1500
Pore volume (ml/g)	1.0–1.1	

Fig. 2. Zeta potential of MN-150 and MN-200 according to works [8,18]. The suspension of microparticles was titrated with either 0.1 M hydrochloric acid or 0.1 M sodium hydroxide.

of significant positive zeta-potential on its surface at pH less than 4.3 was shown (Fig. 2).

Therefore, the aim of this paper was to study the ion-exchange properties of neutral hydrophobic hypercrosslinked polystyrene.

2. Experimental

2.1. Instrumentation

The HPLC system consisted of a model 114 Beckman (Berkeley, CA, USA) high-pressure pump, spectrophotometric detector Micro-UVIS 20 (Carlo Erba, Milan, Italy) and conductometric detector Conductolyser 5300B (LKB, Bromma, Sweden); an air column thermostatic HPLC column oven (CBO industrial electronics, Vena, Austria) with a digital thermometer, Rheodyne (Cotati, CA, USA) Model 7125 injection valve equipped with 100 μl loop and a Spectra-Physics DP-700 integrator (USA). A ZIP (Russia) pH-340 pH meter with glass electrode was used for pH control of eluents.

2.2. Materials

Solutions of perchloric, nitric and sulfuric acids, sodium sulfate (analytical grade, Reakhim, Russia), and sodium perchlorate (HPLC grade, Fisher, Fair Lawn, NJ, USA) in distilled water were used for the preparation of eluents. Water solutions (10 mM) of sodium and potassium salts were used as solutes.

2.3. Columns and sorbents

The hypercrosslinked polystyrene resin chosen for investigation was MN-200 (Purosep-200, Purolite, Pontyclun, UK). The high rigidity and moderate fragility of this polymer allows fine fractions of microparticles of 10–20 μm in size by simple crushing of resin particles of original size 0.1–0.3 mm with pestle and mortar. A combination of sieving through sieves and sedimentation of suspended particles in water or in acetone was used to obtain the final narrow fraction of microparticles of 12–15 μm in size. The stainless steel column 150×3 mm I.D. was slurry packed from acetone under constant pressure.

Another sample of hypercrosslinked polystyrene was an experimental batch of monosize microspherical particles of 10 μm in diameter supplied by Purolite, (Moscow, Russia). This material was slurry packed from acetonitrile into a 250×4.6 mm I.D. stainless steel column.
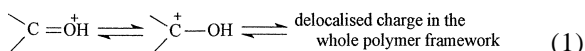
The macroreticular porous PS–DVB resin PRLP-S 300, average particle diameter 8 μm, was obtained from Polymer Labs. (Church Stretton, UK) and was used as a reference polymer adsorbent.
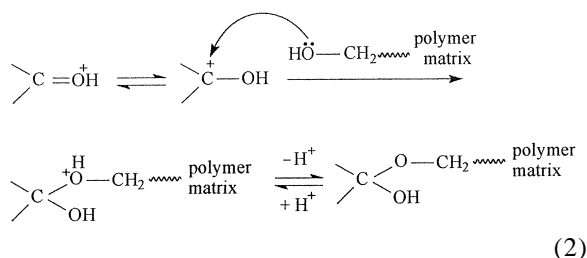
3. Results and discussion

According to the zeta potential curve (Fig. 2), MN-200 may exhibit anion-exchange properties at a pH below 4.3 while maximum positive charge is observed at a pH between 2.5 and 2.7. It should be pointed out that the maximum zeta potential of MN-200 is only 1.5 times lower than for hypercrosslinked polystyrene MN-150 which contains ternary amino groups and has an anion-exchange capacity of 1.06 mequiv./g [8]. However, according to elemental analysis data MN-200 contains only traces of chlorine and a significant amount of oxygen in concentrations between 5 and 6 % (w/w) for the polymer [8]. The exact nature of the functionality on this polymer was determined by the spectroscopic techniques mentioned below. These suggest that the major functional groups are ketones, ethers and

alcohols; however, the complex mixture of groups prevented their quantification. So, the occurrence of significant positive charge at the surface can be attributed only to the presence of oxygen in the framework of this resin. Probably, these positively charged groups are protonated carbonyl groups.

So, it can be proposed that the anion-exchange properties for this "so called" neutral resin attributed to the following possibilities:

$$\begin{array}{c} \begin{array}{c} \\ \\ \end{array}\!\!C = \overset{+}{O}H \rightleftharpoons \begin{array}{c} \\ \\ \end{array}\!\!\overset{+}{C}\!-\!OH \rightleftharpoons \begin{array}{c} \text{delocalised charge in the} \\ \text{whole polymer framework} \end{array} \end{array} \quad (1)$$

The nature of the pH maximum dependence on the zeta-potential for MN-200 is not completely clear. The results of X-ray photoelectron spectroscopy, Fourier transform IR and solid state ^{13}C NMR showed [8] that this polymer has oxygen functionality in the form of carbonyl and non-carbonyl groups. Approximate concentrations of the surface functional groups are presented in Table 2. Three types of cation-exchange groups were found, however, as the surface of HC-PS had positive charge in acidic media. Thus, anion-exchange may occur only on protonated carbonyls. The total concentration of 0.23 mequiv./g corresponds to an oxygen content of approximately 1.3% (w/w). As mentioned above, the polymer contains significantly higher concentrations of oxygen (approx. 5–6 mass percent). The difference can be attributed to ethers or alcohol functional groups, produced by hydrolysis of chloromethyl groups. Probably, at the pH maximum (2.5–2.6) most of the carbonyl groups are already protonated (see Eq. (1)). Therefore, one possible explanation of decreasing zeta-potential of MN-200 in strong acidic solutions is the reversible reaction between protonated carbonyls and OH groups in the structure of polymer with formation of semi-acetals:

Table 2
Concentration of the surface functional groups of MN-200 [8]

Surface groups (mequiv./g)				
Strongly acidic	Weakly acidic	Phenolic	Carbonyl	Total
0.06	0.03	0.01	0.13	0.23

$$\begin{array}{c} \\ \\ \end{array}\!\!C = \overset{+}{O}H \rightleftharpoons \begin{array}{c} \\ \\ \end{array}\!\!\overset{+}{C}\!-\!OH \xrightarrow{} \quad HO\!-\!CH_2\!\!-\!\!\!\sim\!\!\!\!\text{polymer matrix}$$

$$\begin{array}{c} \\ \\ \end{array}\!\!C\!\!\left\langle\!\!\begin{array}{l} \overset{+}{O}\!\!-\!CH_2\!\!\sim\!\!\text{polymer matrix} \\ OH \end{array}\right. \xrightleftharpoons[+H^+]{-H^+} \begin{array}{c} \\ \\ \end{array}\!\!C\!\!\left\langle\!\!\begin{array}{l} O\!-\!CH_2\!\!\sim\!\!\text{polymer matrix} \\ OH \end{array}\right.$$

$$\quad (2)$$

Such reactions are well known for ketones [14]. Thus, as the number of carbonyls decrease this leads to a decrease in positive charge.
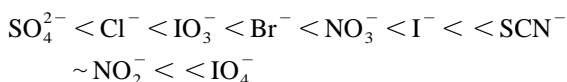
Another possible reason is that with increasing concentration of acid, the polymer beads begin to adsorb anions from the solution. So, the potential of the surface of MN-200 decreases gradually.

3.1. The retention of inorganic anions on MN-200

As discussed above, hypercrosslinked polystyrene should exibit anion-exchange properties within the pH range between 2.0 and 4.3. A number of different inorganic and organic acids can be used as an eluent. Organic acids, especially aromatic acids, are unsuitable because of strong adsorption at the surface of HC-PS. It may lead to formation of system peaks, whose appearance in the chromatogram is considered as a disturbance of the adsorption equilibrium [1]. So, it is more appropriate to use dilute solutions of strong inorganic acids, such as perchloric, nitric and sulfuric, as the eluents.

3.1.1. Influence of the nature and pH of the eluent

Initially, the retention of inorganic anions was investigated at pH 2.6–4.3 using 0.1–4 m*M* perchloric acid as the eluent (Fig. 3a). The retention of all anions is affected by both the concentration of the perchloric acid and the surface charge. The resulting curves present the sum of these factors and have a maximum around pH 3.5 except for nitrite which has a maximum retention at pH 3.0. The obtained retention order was:

$$SO_4^{2-} < Cl^- < IO_3^- < Br^- < NO_3^- < I^- < < SCN^- \sim NO_2^- < < IO_4^-$$

and is different from that generally observed for the common anion exchangers [1,15]. There are two
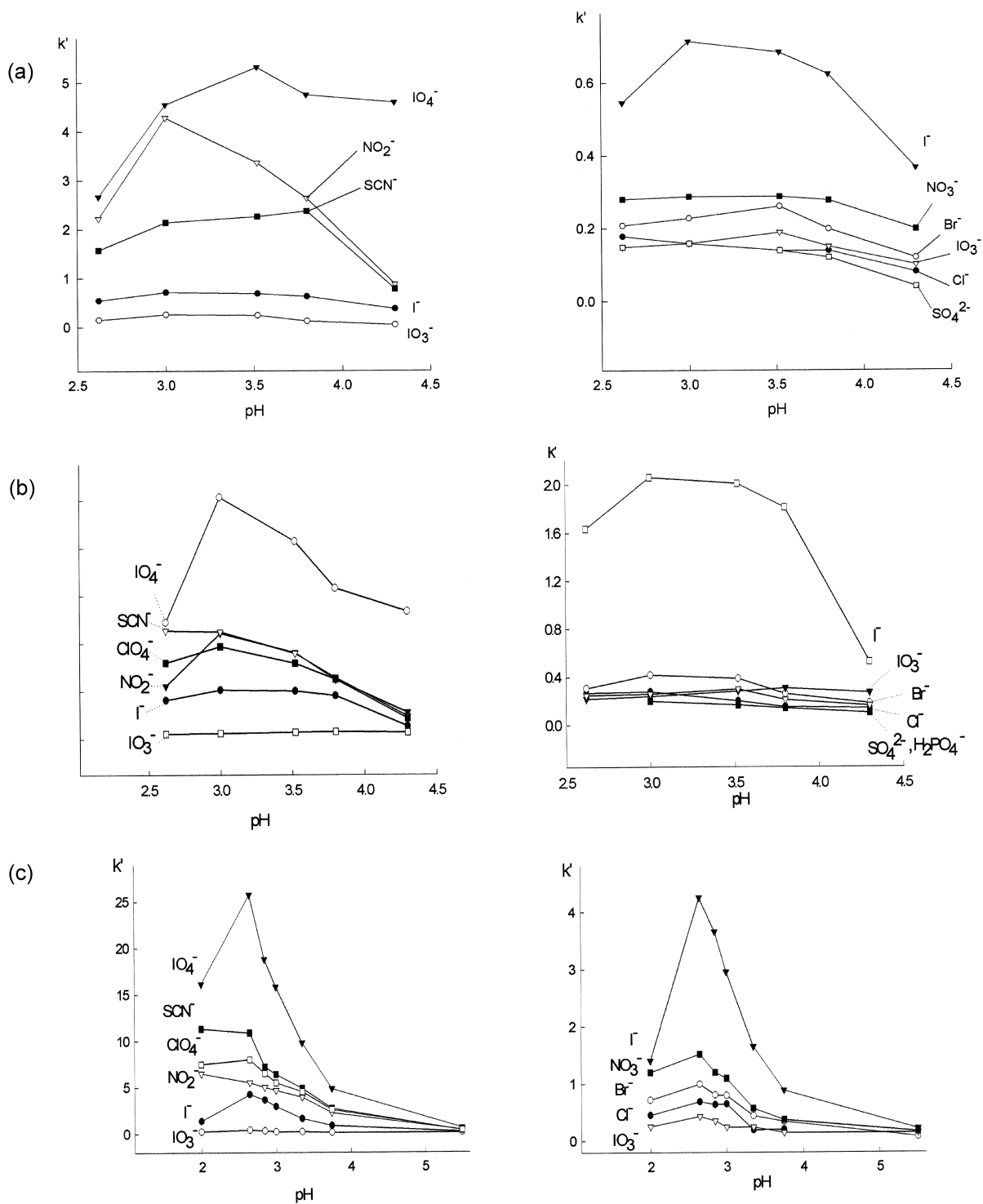
Fig. 3. Plot of capacity factors of some inorganic anions versus pH of mobile phase. Column: MN-200. Eluent: 0.1–4 m*M* perchloric (a), 0.1–4 m*M* nitric (b) and 0.01–4 m*M* sulfuric (c) acid solution. Detection UV 210 nm and conductometric; flow-rate 0.8 ml/min.

features in this retention order. One is very weak retention of sulphate that can shorten the time of analysis of water samples that usually contain sulphate, which is strongly retained on traditional anion exchangers [1,15]. The second difference is a comparatively strong retention of nitrite. This allows separation of the nitrite peak relative to others on the chromatogram.

These results can be explained from the point of view of the complex mechanism of retention of anions. It is well known, that apart from pure ion-exchange processes, non-ionic interactions of ionic species with the stationary phase may occur, especially if the ion-exchange resin used has an aromatic backbone [1]. Generally, such adsorption takes place with polarizable inorganic and organic anions. In some cases, even the ion-exchange separation of simple inorganic anions such as bromide and nitrate is strongly affected by non-ionic sorption properties [1]. In the case of MN-200, the combination of high hydrophobicity and the presence of different functionality types on the surface and anion-exchange properties due to a positively charged surface results in an unusual elution order. Being in neutral form due to protonation (pK_a $HNO_2 = 3.4$) nitrite is strongly retained at low pH of the eluent due to specific interactions with the surface of hypercrosslinked polystyrene. Probably, nitrous acid reacts with residual hydroxyl groups on the HC-PS surface with the formation of ester.

$$\text{polymer matrix}\text{\large\char`\~}OH + HNO_2 = \text{polymer matrix}\text{\large\char`\~}ONO + H_2O \qquad (3)$$
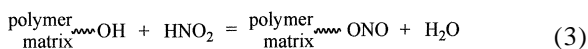
It is difficult to find direct evidence of such a process but the formation of nitrite ester from a mixture of nitrite and alcohol in acidic solution has been verified by gas chromatography and UV spectrophotometry [16]. However, it is more difficult to find a reasonable explanation for such strong retention of this anion on MN-200 at pH 4.3. At this pH nitrite is still retained stronger than thiocyanate. The similar affinity to nitrite was found for PS–DVB in additional experiments performed with a PLRP-S column. In an acid eluent (pH 2.85) the neutral PLRP-S resin retains only a few anions while nitrite was retained much stronger ($k' = 0.92$) than such hydrophobic anions as thiocyanate ($k' = 0.08$) and

periodate ($k' = 0.10$). It means the existence of special affinity of PS–DVB resin to nitrite.

As discussed above, there are many functional groups on the surface of HC-PS (Table 2), not only positively, but also negatively charged in the experimental pH range [8]. Therefore, the higher charge of anion results in its stronger repulsion. It could be a possible explanation for the weak retention of divalent sulphate. So, the retention mechanism of inorganic anions, except for nitrite, is mainly ion exchange.

According to the obtained retention order of anions for HC-PS the elution ability of inorganic acids used as the eluents should be: $H_2SO_4 <$ $HNO_3 < HClO_4$. To investigate the role of the nature of the eluent on selectivity, the retention of inorganic anions was studied in the pH range from 2.0 to 4.3 with diluted nitric and sulfuric acids as the eluents (Fig. 3b and c). The retention of anions grows with the decrease of elution ability of the acid. This effect is considerably higher for the strongly retained anions such as I^-, IO_4^-, SCN^-, ClO_4^-, than for the less retained $H_2PO_4^-$, Cl^-, Br^-, NO_3^-, IO_3^-. For example, k' of IO_4^- at pH 3.0 is three times higher for nitric acid eluent and five times higher for sulfuric acid eluent than for elution with perchloric acid. It should be noted, the change of the nature of the eluent has insignificant influence on the retention of nitrite at pH < 3.5. Therefore, its retention mechanism is different from other studied anions. Formation of esters on the surface of HC-PS (3) is most likely the main contribution in the retention of nitrite. At pH values higher than 3.5 the regularity of retention of NO_2^- is similar to that for other anions.

The maximum dependence of k'–pH shifts to lower pH with reducing elution ability of the eluent. It is in the pH range 3.5–3.7 for elution with perchloric acid and at pH 3.0 with nitric acid. For sulfuric acid, the maximum retention of anions is observed at pH 2.6 corresponding to the maximum value of zeta-potential of sorbent. Further pH decreases result in decreases in k' of all anions except for nitrite. Thus, the character of k'–pH dependence depends on the affinity of the eluting anion for the surface of HC-PS.

In further experiments on MN-200, dilute sulfuric acid was used as the eluent because of the stronger
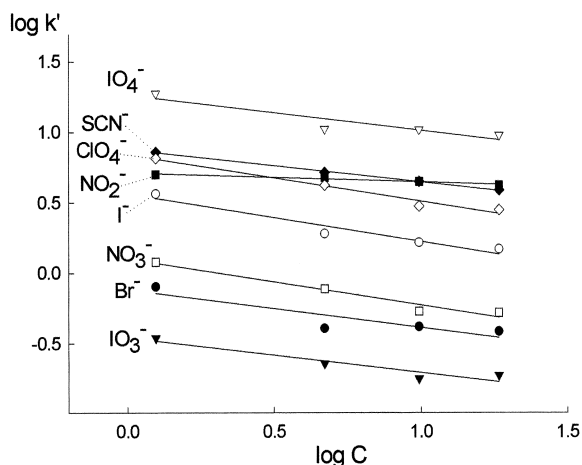
Fig. 4. Effect of ionic strength on the retention of inorganic anions. Column: MN-200. Eluent: 1.25 mM H$_2$SO$_4$–Na$_2$SO$_4$, pH 2.8. Detection UV 210 nm and conductometric; flow-rate 0.8 ml/min.

retention of anions. In this case, all regularities were outlined sharply.

3.1.2. Effect of ionic strength

In addition to the type of eluent, its ionic strength is one of the important parameters affecting the retention of anions. To study the influence of this parameter on the retention on MN-200, the con-

centration of sodium sulfate was varied at constant pH values of the eluent (Fig. 4). The retention of anions decreases with the increase of eluent concentration. Linear dependences log k' – log C(sulfate) were obtained for all the inorganic anions under investigation. Their slopes are about 0.28 for mono-charged anions except for nitrite. Thus, the ionic strength has an insignificant effect on its retention.

3.1.3. Effect of temperature

It has been established, that the temperature has little influence on retention of anions in the case of "pure" ion exchange [1]. For mixed-mode mechanisms, investigation of the thermodynamics of adsorption could provide additional data for understanding them better. The capacity factor is directly connected to the distribution coefficient, and thus with thermodynamic functions:

$$\ln k' = \frac{-\Delta H}{RT} + \frac{-\Delta S}{R} + \ln \phi \qquad (1)$$

where ΔH is enthalpy change of the ion exchange, ΔS is sorption entropy, and ϕ is the phase ratio, a characteristic constant for a given column. The influence of the column temperature on the retention of inorganic anions was investigated in the range from 20 to 67°C (Fig. 5). The experimental regularities of log k' vs. reciprocal temperature are
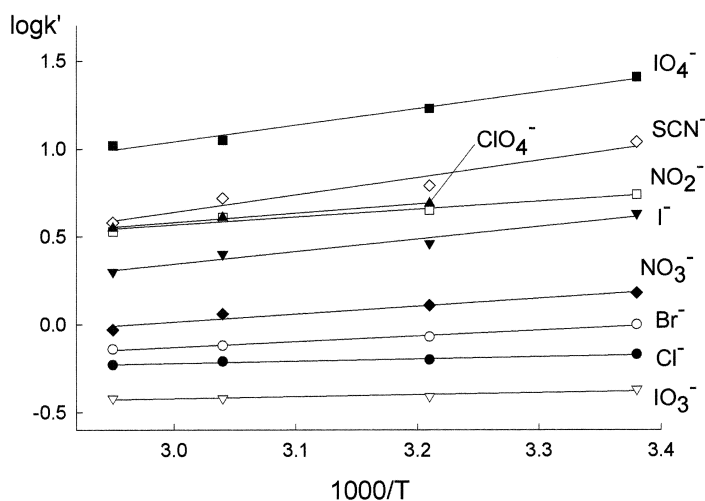

Fig. 5. Effect of column temperature on the retention of inorganic anions. Column: MN-200. Eluent: 1.25 mM H$_2$SO$_4$, pH 2.8. Detection UV 210 nm and conductometric; flow-rate 0.8 ml/min.

Table 3
Adsorption heats ($-\Delta H$, kJ/mol) of inorganic anions on MN-200; eluent: H_2SO_4

Anions	pH 2.8	pH 3.5
IO_3^-	2.19 ± 2.02	2.75 ± 2.87
Cl^-	2.46 ± 1.59	-1.74 ± 3.24
Br^-	6.24 ± 2.22	3.29 ± 5.05
I^-	13.7 ± 8.28	4.54 ± 4.29
NO_3^-	8.65 ± 4.39	1.51 ± 0.96
NO_2^-	8.60 ± 3.59	10.8 ± 8.61
ClO_4^-	10.1 ± 4.43	
IO_4^-	18.0 ± 5.3	
SCN^-	18.9 ± 9.3	8.81 ± 4.40

linear for all anions under investigation. Calculated values of adsorption heats are presented in Table 3. The values of adsorption heats for bromide and nitrate on MN-200 are of the same order as on IonPac AS3 (8.6 and 8.1 kJ/mol, respectively [1]). However, in the case of chloride, nitrite and phosphate, the k' values on IonPac AS3 were found to be constant within experimental error limits in the temperature range investigated [1]. This means their $-\Delta H$ is negligible. At the same time, $-\Delta H$ values of these anions on MN-200 are remarkably higher. To check the mechanism, the adsorption heats of anions were calculated with sulfuric acid as the eluent at pH 2.8 and 3.5. Increase in the pH of the eluent results in considerable decreases of adsorption heats due to lower sorbent capacity. It should be noted, that calculated adsorption heats for all anions under the conditions investigated are in the range from -2 to 19 kJ/mol. It is well known, that changes in adsorption heat values of ion-exchange processes usually does not exceed 25 kJ/mol for mono- and divalent ions [17]. So, another confirmation for mainly an ion-exchange retention mechanism was obtained. Increasing temperature improves column efficiency, probably, due to better adsorption–desorption kinetics.

In spite of the good anion-exchange selectivity of MN-200, the efficiency of the chromatographic column used in these experiments was relatively poor (about 800 theoretical plates per meter) and allowed the separation of only four anions (Fig. 6). However, a further improvement of efficiency and resolution ability of the column can be achieved with
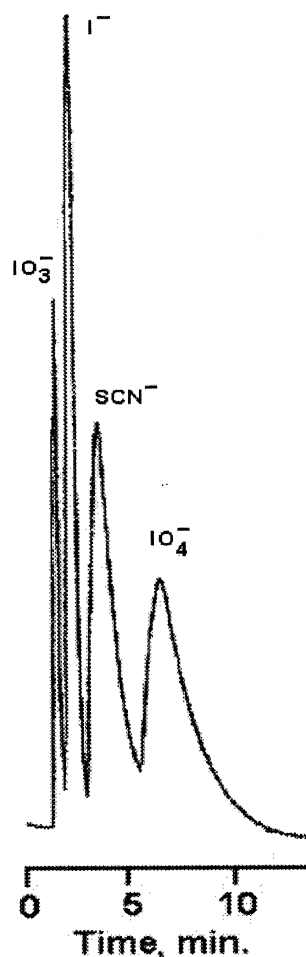

Fig. 6. Chromatogram of mixture of inorganic anions. Column 150×3 mm I.D., 12–15 μm MN-200. Eluent: 1.25 m*M* sulfuric acid. Detection UV 210 nm; flow-rate 0.8 ml/min.

the use of narrow, fine spherical particles of neutral hydrophobic HC-PS

3.2. The retention of inorganic anions on monosized spherical HC-PS

To ensure similar properties, a mainly positively charged surface for synthesized spherical HC-PS particles the retention of inorganic anions as a function of pH of eluent, was studied under constant ionic strength of the eluent. The resulting k'–pH
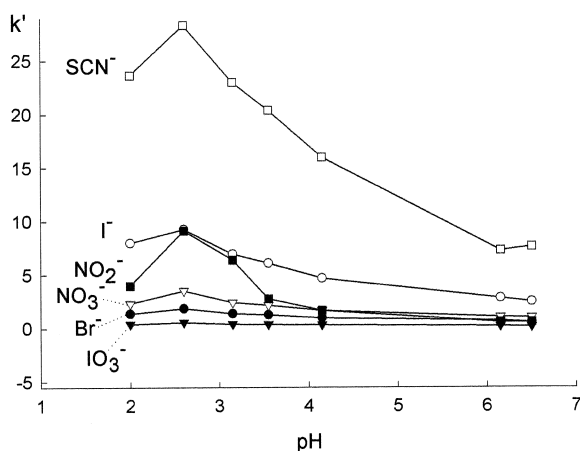
Fig. 7. The retention of inorganic anions versus pH of mobile phase at constant ionic strength. Column: 250×4.6 mm I.D., 10 μm spherical HC-PS. Eluent: $\Sigma C(H_2SO_4 + Na_2SO_4) = 7.5$ mM. Detection UV 210 nm; flow-rate 1.5 ml/min.

Fig. 8. The retention of inorganic anions versus pH of mobile phase. Column: 250×4.6 mm I.D., 10 μm spherical HC-PS. Eluent: 0.05–10 mM perchloric acid solution. Detection conductometric; flow-rate 1.5 ml/min.

dependence should be strongly correlated with the profile of the change of zeta-potential with pH of the eluent. In fact, the dependence obtained (Fig. 7) has the maximum in the same pH range as the zeta-potential curve of MN-200. Comparatively strong retention of polarizable anions I^- and SCN^- at pH higher than 4.3 was observed, probably because of hydrophobic interactions with the matrix of hyper-crosslinked polystyrene.

The retention of all anions on new resin is much stronger than on original sample of MN-200, probably due to higher concentration of carbonyls on the surface. With sulfuric acid as the eluent, low performance and non-symmetrical peaks are observed. So, there is an additional possibility of using a stronger eluent such as perchloric acid that provides a better peak shape. Fig. 8 shows the effect of the pH of perchloric acid on the retention behavior of a number of inorganic anions. As mentioned above, the retention of anions on HC-PS is a sum of two factors: surface charge and the concentration of the eluent. The obtained dependence can be divided in two parts. The growth of retention at the first part of the dependence in the pH range from 2.0 to 4.3 can be attributed mainly to a decrease in the concentration of the eluent while the charge of the surface decreases starting from pH 2.5. Further increase in
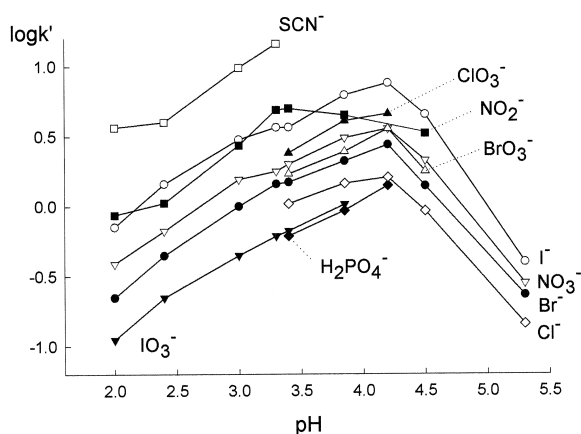
pH results in a decrease in retention because the sorbent becomes negatively charged at pH values higher than 4.3. Hence, the surface repels anions and their retention decreases. The maximum of retention was observed at pH 4.2 that corresponded to a ''zero charge'' point of HC-PS.

The dependence of retention of anions on the ionic strength of the eluent was also investigated . The log $k' - \log C$ dependence is linear for all anions. The related slopes depend on the charge of eluent and analyte ion and are equal to 0.28 and 0.74 for sulfate and perchlorate based eluents, respectively, while according to theory these values should be 0.5 and 1 [1]. On the one hand, functional groups on the surface of HC-PS participate in different equilibrium processes, so the effective charge of anion-exchange groups could be less than 1. Therefore, the slopes of log $k' - \log C$ dependence could be less than theoretical ones. On the other hand, repulsion from negatively charged groups on the sorbent surface may occur. The repulsion for divalent sulfate is stronger than for monovalent perchlorate. So, the former has weak elution ability and the influence of its concentration on the retention is less expressed. This may be a reason for stronger deviation of the slope for sulfate eluent from theoretical value, than for perchlorate one.
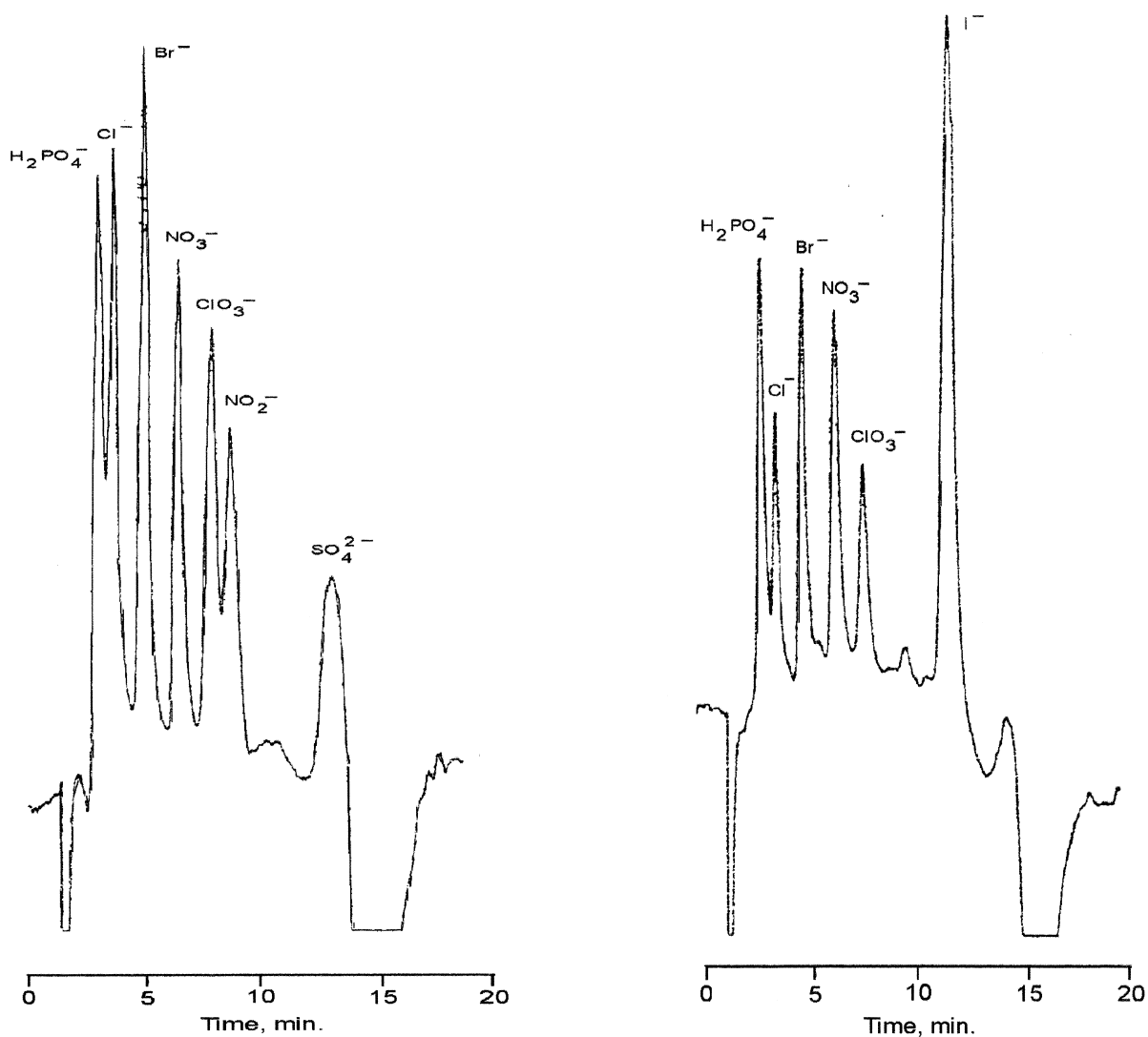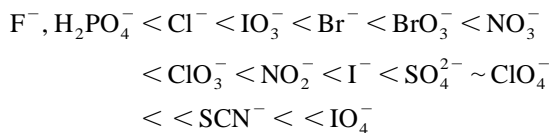
Fig. 9. Chromatograms of mixtures of inorganic anions. Column: 250×4.6 mm I.D., 10 μm spherical HC-PS. Eluent: 0.2 mM perchloric acid solution. Detection conductometric; flow-rate 1.5 ml/min.

In the whole, the selectivity of spherical HC-PS material is similar to that observed for MN-200:

$$F^-, H_2PO_4^- < Cl^- < IO_3^- < Br^- < BrO_3^- < NO_3^-$$

$$< ClO_3^- < NO_2^- < I^- < SO_4^{2-} \sim ClO_4^-$$

$$< < SCN^- < < IO_4^-$$

The most efficient and selective separation of inorganic anions on HC-PS was achieved with 0.2 mM HClO$_4$ (Fig. 9). The calculated number of theoretical plates was only about 3400 per meter. However, it allowed separation of 6–7 anions.

4. Conclusions

The evidence for the existence of a positively charged surface on HC-PS materials was demonstrated and possible reasons for it were discussed.

The new type of anion-exchange selectivity associated with positive charge localized in the framework of the neutral hypercrosslinked resins was found. Protonated carbonyls were shown to be mostly responsible for anion-exchange properties of HC-PS.

The retention mechanism of inorganic anions on HC-PS was proved to be mainly by ion-exchange except for retention of nitrite which is strongly retained due to the formation of an ester linkage with residual OH groups at the surface of this resin. Repulsion from negatively charged groups in the structure of HC-PS also occurs that results in an unusual retention order of anions. The retention mechanism also includes hydrophobic interactions in the case of polarizable anions.

The possible application of HC-PS as an anion-exchanger is considered.

Acknowledgements

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