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New Polymeric Sorbents with Increased Hydrophilicity for Ionic Chromatography

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Abstract—To increase the efficiency of anion exchangers based on a copolymer of styrene and divinylbenzene, a new method of covalent attachment of quaternary ammonium functional groups of various hydrophilicity that uses 1,4-butanediol diglycidyl ether to increase their spatial distance from the matrix has been suggested. Synthesis includes acylation of the matrix with acetic anhydride, reductive amination, alkylation of the aminated phase with 1,4-butanediol diglycidyl ether, and amination with trimethylamine and dimethylethanolamine of terminal oxirane ring. The use of dimethylamine and methylamine hydrochlorides for the reductive amination makes it possible to obtain a linear or branched structure of the ion exchange layer, respectively. The obtained anion exchangers make it possible to determine 7 inorganic anions simultaneously (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}) in suppression ion chromatography mode, and the anion exchanger with the branched structure and hydrophilic functional group has demonstrated the highest efficiency (31000 and 35000 theoretical plates/m in relation to Br^- and NO_2^-, respectively).

Keywords: anion exchangers, ion chromatography, polystyrene—divinylbenzene, determination of anions
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INTRODUCTION

High-performance and selective determination of inorganic anions is a task of current importance in modern ion chromatography; therefore, the development of new anion exchange sorbents is one of the most important and promising research areas. When anion exchangers based on a copolymer of styrene—divinylbenzene (PS—DVB) are used, not only theion exchange, but also the nonion-exchange, in particular hydrophobic π–π and anion-π-interactions, can contribute to the retention of anions [1–3], which is a cause of anomalous retention of polarizable anions such as nitrate, bromide, and nitrite, as well as to the low efficiency of columns [4]. The following approaches to the reduction of interaction of anions with the matrix and to increase the efficiency of anion exchangers at the stage of synthesis of ion exchangers are known: an increase of the spatial distance of functional groups (FG) from matrix and an increase of sorbent hydrophilicity by the addition of hydrophilic fragments to the structure of the ion exchange layer and FG.

From this point of view, the use of diepoxy compounds, which represent diglycidyl ethers possessing a high reaction ability in reactions with amines, is promising for the preparation of highly efficient sorbents. The application of such compounds makes it possible to combine hydrophilization and spacial distancing of the functional group, since the ethers can play the role of hydrophilic spacers for covalent attachment of FG and make it possible to create a branched structure of an ion exchange layer containing hydrophilic hydroxy groups, which shields the aromatic basis of the sorbent [5–8]. The selection of tertiary amine to open the oxirane cycle determines the structure of terminal quaternary ammonium FG. Thus, variation of structure of the whole ion exchange layer and, consequently, control of the efficiency and selectivity of the obtained sorbents are possible as a result of the selection of the method of FG attachment to the matrix and amine structure.

Diglycidyl ethers have recently been widely used for the creation of a hyperbranched hydrophilic anion exchange layer to increase the selectivity of anion exchangers. The following methods of attachment of these layers to the matrix surface are possible: electrostatic and covalent. The first version is presented in [6], in which the authors used methylamine and 1,4-butanediol diglycidyl ether for the creation of a polycation and attached it electrostatically to the surface of a negatively charged sulfonated polymer based on ethylvinylbenzene and divinylbenzene. Thereafter, several anion exchange layers were built up on a polycation containing substituents with terminal epoxide rings in its structure by alternating amination and alkylation reactions. It was demonstrated that sorbent capacity increases, selectivity to singularly charged anions increases, and the contribution of hydrophobic interactions in their retention decreases with an increase of the number of diepoxide–methylamine cycles.

Covalent attachment of a hyperbranched anion exchange layer is possible when electron donor groups are present on the sorbent surface. This approach is easily carried out on silica gel, for which simple methods of covalent attachment of epoxide rings or amino groups suitable for the further buildup of ion exchange layer on the surface are known. For example, the authors of [9, 10] used 1,4-butandiol diglycidyl ether and primary amines (aniline and methylamine) for the successive buildup of layers on silica gel preliminary treated with aminopropyltrioxysilane. In [5] methylamine and 1,4-butandiol diglycidyl ether were used for the covalent attachment of a hyperbranched anion exchange layer on the surface of a polymer based on 1,4-di-(2-hydroxy-3-metacryloxypropoxy)phenol; as a result, sorbents containing 3, 5, 7, and 11 layers with quaternary ammonium groups were obtained. As in the case of electrostatic attachment, an improvement in the selectivity of the sorbent with an increase in the quantity of layers is observed upon covalent modification. Moreover, this method of synthesis makes it possible to affect the selectivity of the anion exchanger by varying the structure of ether or amine [6, 9].

It should be mentioned that examples of covalent attachment of such layers, as well as singular FG using diepoxides on PS—DVB, are not presented in publications; however, this method seems to be promising from the point of view of the possibility of an increase int he effectiveness and control of selectivity of separation.

The goal of the present work is the preparation of new covalently bonded anion exchangers that use 1,4-butandiol diglycidyl ether to increase spatial distance of the FG formed by amines of various hydrophilicity, as well as the study of their chromatographic properties in isocratic and gradient modes of suppression ion chromatography with hydroxide as eluent.

EXPERIMENTAL CONDITIONS

Equipment and materials. The experiments were performed on a Dionex ICS 3000 ion chromatograph (Thermo Scientific, United States) using a hydroxide eluent with a flow rate of 0.5 mL/min. The acquisition and processing of chromatographic data were performed with Chromeleon 6.8 software (Thermo Scientific, United States).

A copolymer of styrene and divinylbenzene with a 50% degree of crosslinking, 3.3 ± 0.2 μm particles diameter, with a surface area 200 m^2/g, a total pore volume of 0.64 cm^3, and an average pore diameter of 6 nm was, used as the matrix (Laboratory of Chromatography, Department of Chemistry, Moscow State University).

The following reagents were used for modification of the matrix:

$AlCl_3$, analytical grade (Aldrich, United States), $(CH_3CO)_2O$ (Aldrich, United States), CS_2 (99.9%) (Acros Organics, Belgium), $NaBH_3CN$ (Aldrich, United States), $CH_3NH_2 \cdot HCl$ (Aldrich, United States), $(CH_3)_2NH \cdot HCl$ (99%) (Aldrich, United States), EtOH analytical grade (Labtekh, Russia), 1,4-butandiol diglycidyl ether (≥95%) (Aldrich, United States), NaOH cp grade (Khimmed, Russia), HCl cp grade (Khimmed, Russia), $(CH_3)_3N$ (45% solution) (TMA) (Aldrich, United States), dimethyletanolamine (DMEA) (99.5%) (Aldrich, United States).

The following reagents were used for preparation of solutions of the determined components: $(NH_4)_2SO_4$, $NaNO_2$, Na_2HPO_4, KBr, KNO_3, NH_4Cl (all of analytical grade), and NaF cp grade (all from Khimmed and Labtekh, Russia). Stock 10 mM solutions of salts were prepared by dissolving their precise weights. Working solutions with a lower concentration were obtained by dilution of the stock solutions.

RESULTS AND DISCUSSION

Synthesis of anion exchangers. For covalent attachment of FG using 1,4-butandiol diglycidyl ether on the surface of the polymeric matrix, the preliminary incorporation of electron donor substituents in its structure is needed, in particular, amino groups, which easily react with epoxides even at room temperature. Many methods are described in the publications [11–14], making it possible to introduce amino groups in the PS–DVB structure; however, the scheme presented in [15–18], which includes acylation of a matrix with acetic anhydride with a subsequent reduction amination, appeared to be the optimum method. This method makes it possible to avoid the occurrence of side reactions, and, depending on the used amine (methylamine or dimethylamine), makes it possible to obtain both secondary and tertiary amino groups suitable for further modification. Thus, it is possible to obtain ion exchange layers of various structures and hydrophilicities by the selection of the reagent for the reduction amination. After alkylation of the amino groups by diglycidyl ether, the use of various tertiary amines to open the oxirane cycle is possible. This allows an increase in the hydrophilicity of the sorbent. In the present work, dimethylamine hydrochloride and methylamine hydrochloride were used for reductive amination, which makes it possible to obtain a more branched structure of the ion exchange layer, and trimethylamine and dimethylethanolamine were selected to study the effect of FG hydrophilicity on chromatographic properties.

The scheme of the synthesis and most probable structure of the obtained anion-exchangers are presented in Fig. 1, and the reaction conditions selected

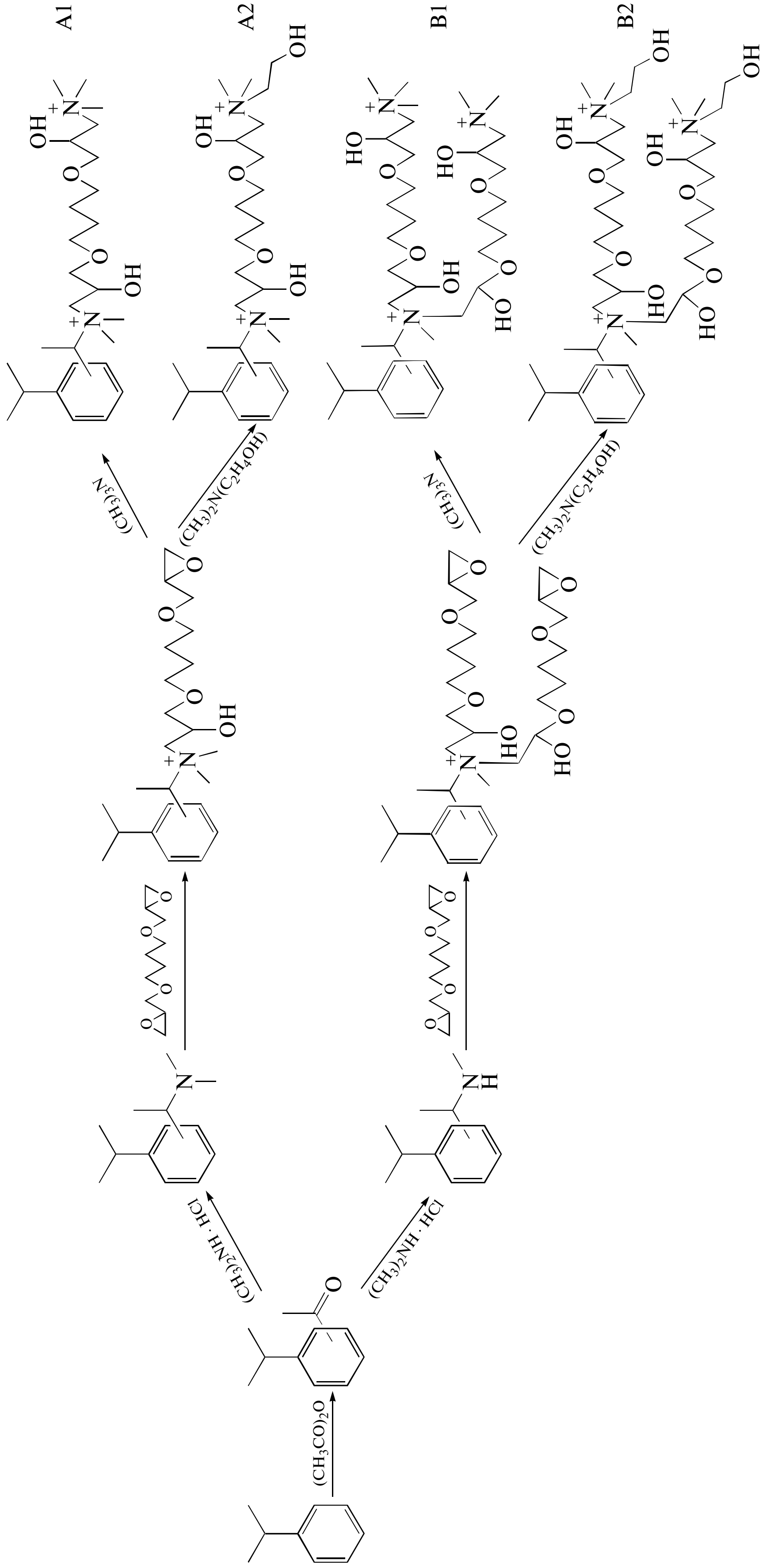

Fig. 1. Scheme of synthesis of anion exchangers.

Table 1. Conditions of synthesis and ion-exchange capacities of the obtained sorbents

Sorbent	Acylation with acetic anhydride	Reductive amination with dimethylamine hydrochloride	Reductive amination with methylamine hydrochloride	Alkylation with 1,4-butanediol diglycidyl ether	Amination with TMA	Amination with DMEA	Capacity, mmol/g**
A1	0.01* 42°C 5 h	0.006* 50°C 16 h	–	0.012* 50°C 3 h	0.012* 50°C 3 h	–	0.054 ± 0.005
A2		0.006* 50°C 16 h	–	0.012* 50°C 1 h	0.012* 50°C 3 h	–	0.067 ± 0.007
B1		–	0.012* 50°C 16 h	0.012* 50°C 3 h	–	0.012* 50°C 3 h	0.019 ± 0.002
B2		–	0.012* 50°C 16 h	0.012* 50°C 1 h	–	0.012* 50°C 3 h	0.036 ± 0.004

* Quantity of reagent (mol) per 1 g of matrix.

** Error of determination with ion chromatography ($n = 3$, $P = 0.95$).

with the goal of generating ion exchange capacity in a rangeof 0.02–0.08 mmol/g, which make it possible to work in the suppression ion chromatography mode, are presented in Table 1. The method presented in [15] was used to determine capacities.

Study of chromatographic properties of anion exchangers. The chromatographic properties of all synthesized anion exchangers were studied in suppression ion chromatography mode by elution with KOH solutions. For the obtained anion exchangers, the conditions of rapid and selective separation of a mixture of seven inorganic anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate) were selected.

The anion exchangers A1 and A2 with nonbranched structure of the ion exchange layer with trimethylammonium and dimethyl ethanol ammonium FG respectively were initially synthesized with the use of dimethylamine hydrochloride for the reduction amination. These sorbents have two ion exchange centers in the structure of the ion exchange layer (Fig. 1). Since the capacities of the obtained sorbents are close, both sorbents were tested under similar conditions with 5 mM KOH as eluent for a comparison of chromatographic properties, in particular, selectivity (Fig. 2).

The retention order of anions for the given anion exchangers corresponds to conventional ion chromatography, in which singularly charged anions are eluted before the doubly charged; however, with an increase of hydrophilicity of FG in passing to sorbent A2, a certain decrease of relative retention of the polarizable anions (most noticeably for the nitrate and bromide ions) is observed. It also should be noticed that sulfate is retained significantly worse on the sorbent with a hydrophilic DMEA group than on the sorbent with a hydrophobic TMA group. This is associated with an increase in the degree of FG hydration with an increase of its hydrophilicity and, as a consequence, with an increase in the affinity of the eluent hydrated ions, which results in an increase of the elution strength of hydroxide ion in transition from sorbent A1 to sorbent A2 [19].

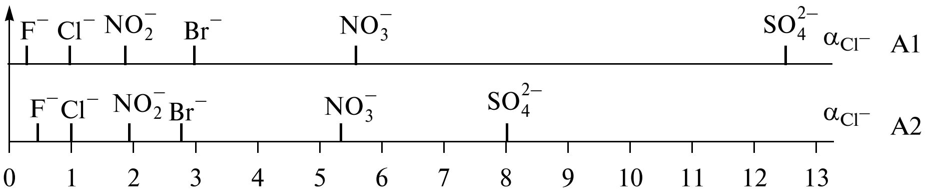

Fig. 2. Selectivity scales for sorbents A1 and A2, eluent 5 mM KOH, $F = 0.5$ mL/min.

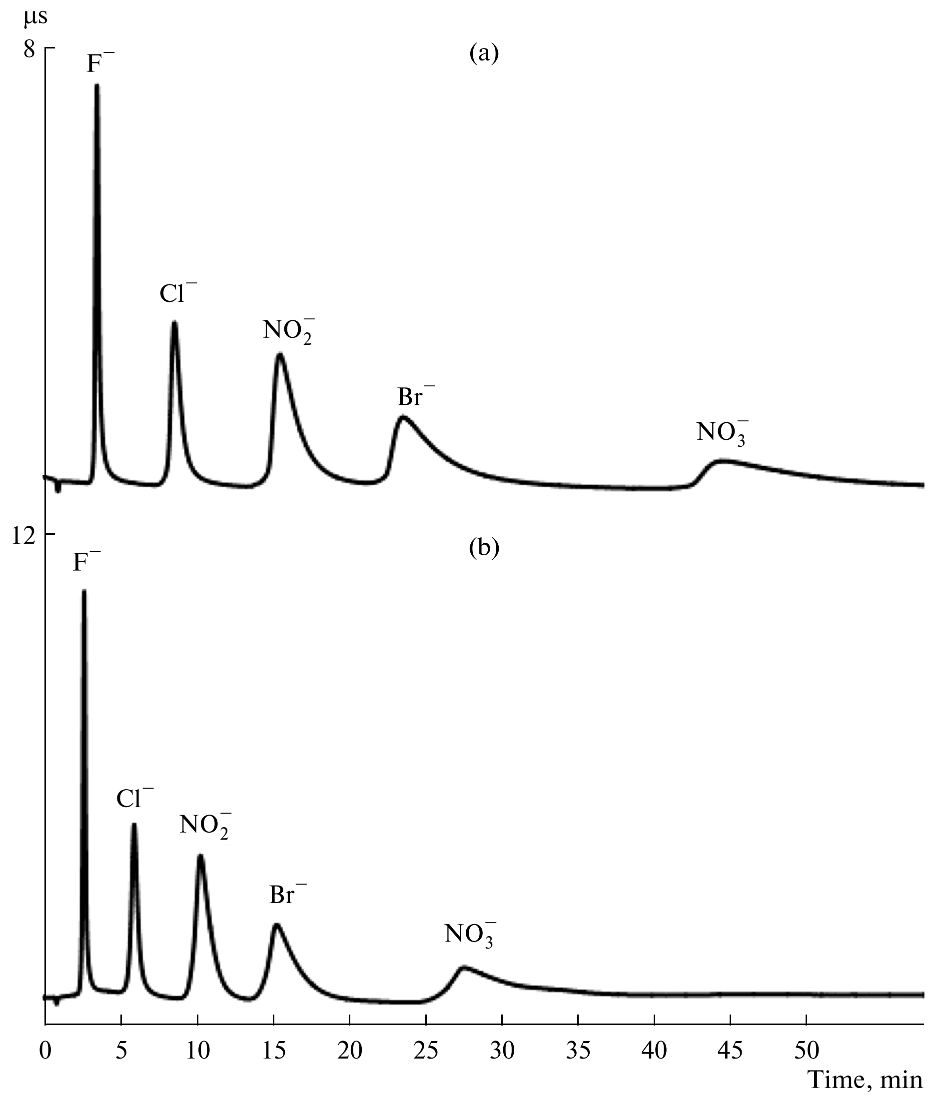

Fig. 3. Chromatograms of mixture of inorganic anions in isocratic elution mode (eluent 5 mM KOH, $F = 0.5$ mL/min): a, sorbent A1, b, sorbent A2.

A decrease in the nonion-exchange, particularly hydrophobic interactions of the polarizable anions with the matrix, as well as an increase of elution strength of a hydroxide ion with an increase of FG hydrophilicity, provides higher speed of separation, despite the higher capacity of sorbent A2 as compared to sorbent A1. Thus, when 5 mM KOH is used as eluent on sorbent A1 with hydrophobic FG, no less than 50 min are needed for the separation of a mixture of five singularly charged inorganic ions (fluoride, chloride, nitrite, bromide, and nitrate), while a significant erosion of the peaks of polarizable bromide and nitrate ions is observed (Fig. 3a). On A2 sorbent under the same conditions, this mixture can be separated in less than 35 min (Fig. 3b). However, a rather low efficiency in relation to the polarizable ions is characteristic for sorbent A2 as well (Table 2). The symmetry of the peaks, however, does improve compared to sorbent A1 (Table 3), which can be associated with a decrease of the contribution of hydrophobic interactions with an increase in the hydrophilicity of FG.

As it is seen from Table 2, the best values of efficiency in relation to the polarizable nitrite and bromide ions on the A2 sorbent with more hydrophilic FG are only 12000 and 9000 theoretical plates/m, respectively, which are significantly lower than the efficiency of the modern commercial anion exchange sorbents. Such low efficiency may be associated with insufficient shielding of the polymeric matrix and, as a consequence, with its significant effect on the retention of anions.

Sorbents B1 and B2 with a branched structure of the ion exchange layer were obtained with the goal of greater shielding of the matrix surface. For this, meth-

Table 2. Retention factors and column efficiency in relation to inorganic anions for sorbents A1, A2, B1, and B2 with 5 mM KOH as eluent

Sorbent / Anion	A1		A2		B1		B2	
	k'	$N \times 10^{-3}$, tp/m	k'	$N \times 10^{-3}$, tp/m	k'	$N \times 10^{-3}$, tp/m	k'	$N \times 10^{-3}$, tp/m
F^-	2.2	29.0	1.7	33.0	1.2	29.0	1.0	35.0
Cl^-	6.6	20.0	4.8	23.0	2.4	21.0	1.8	40.0
NO_2^-	12.7	11.0	8.9	12.0	4.0	14.0	2.7	35.0
Br^-	19.6	8.0	13.6	9.0	5.4	18.0	3.3	31.0
NO_3^-	37.7	7.0	25.3	8.0	9.5	10.0	4.8	19.0
SO_4^{2-}	83.2	20.0	38.3	15.0	13.1	17.0	9.0	15.0

ylamine hydrochloride was used at the stage of reductive amination, and TMA and DMEA respectively were used for amination.

The retention order of anions when 5 mM KOH was used as eluent for the given anion exchangers also corresponds to the conventional order for ion chromatography (Fig. 4), and a decrease of the relative retention of the polarizable anions due to a decrease of non-ion-exchange interactions is observed with an increase in FG hydrophilicity, as well as of the sulfate ion, which is caused by an increase of elution strength of hydroxide ion.

On sorbent B1, the separation of a mixture of six anions (fluoride, chloride, nitrite, bromide, nitrate, and sulfate) is possible in 16 min in isocratic mode, and on sorbent B2 it is possible to separate seven anions, including triple-charged phosphate, in the same time (Fig. 5). Comparison of the chromatographic characteristics of the anion exchangers B1 and B2 when 5 mM KOH is used as eluent (Table 2) shows a significant increase of efficiency in relation to the polarizable ions with an increase in FG hydrophilicity. Thus, on sorbent B1 the values of efficiency in relation to the polarizable nitrite and bromide ions attain only 14000 and 18000 theoretical plates/m, while on sorbent B2 with more hydrophilic FG these the values are 35000 and 31000 theoretical plates/m, respectively. The significant growth of efficiency and the improvement of peak symmetry in transition from sorbents with a linear structure (A1 and A2) to similar sorbents with the branched structure (B1 and B2) is also worth noting. This is associated with a decrease in the non-ion-exchange interactions of the polarizable anions with the matrix due to shielding of the aromatic basis of sorbent by the branched structure of the ion exchange layer.

Table 3. Asymmetry coefficients for sorbents A1, A2, B1, and B2 using 5 mM KOH as eluent

Sorbent / Anion	A1	A2	B1	B2
F^-	1.7	1.3	1.3	1.3
Cl^-	1.7	1.3	1.3	1.1
NO_2^-	2.1	1.6	1.4	1.1
Br^-	3.0	1.9	1.5	1.3
NO_3^-	2.9	1.9	1.3	2.0
SO_4^{2-}	1.3	1.2	1.3	1.8

An increased speed of analysis and separation of seven standard inorganic anions on the obtained anion exchangers is possible with a transition to the gradient mode of elution. In the gradient mode, the separation of a mixture of seven anions is possible on sorbent A2 in 18 min, while on sorbent B2 the same mixture of anions can be separated in 9 min (Fig. 6). It should be noted that, even in this case, strong peak broadening is observed on A2 sorbent as compared to sorbent B2.

To evaluate the matrix effect on the retention of polarizable anions on the B1 and B2 sorbents, the mechanism of anion retention was studied. When there are no side interactions, i.e. with anion retention only by the ion exchange mechanism, the curve of the $\log k'$–$\log c$ relationship represents a straight line with a slope equal to the ratio of charges of the eluted and eluting ions [20]. To find the dominant mechanism of anion retention on the anion exchangers B1 and B2, the dependencies of the logarithm of the capacity coefficient of the determined components on the logarithm of concentration of eluent were constructed (Figs. 7, 8). The range of eluent concentrations for sorbent B1 was from 11 to 17 mM KOH, and it was from 5 to 11 mM KOH for sorbent B2. In Table 4 the equations describing the dependence of the anion retention factor on the concentration of eluents, as well as the coefficients of the confidence of approxi-

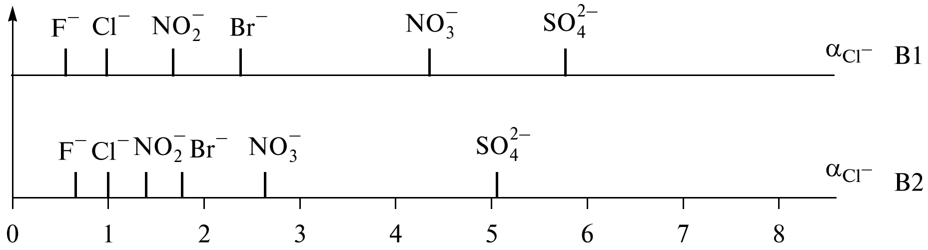

Fig. 4. Selectivity scales for sorbents B1 and B2 (eluent 5 mM KOH, $F = 0.5$ mL/min).

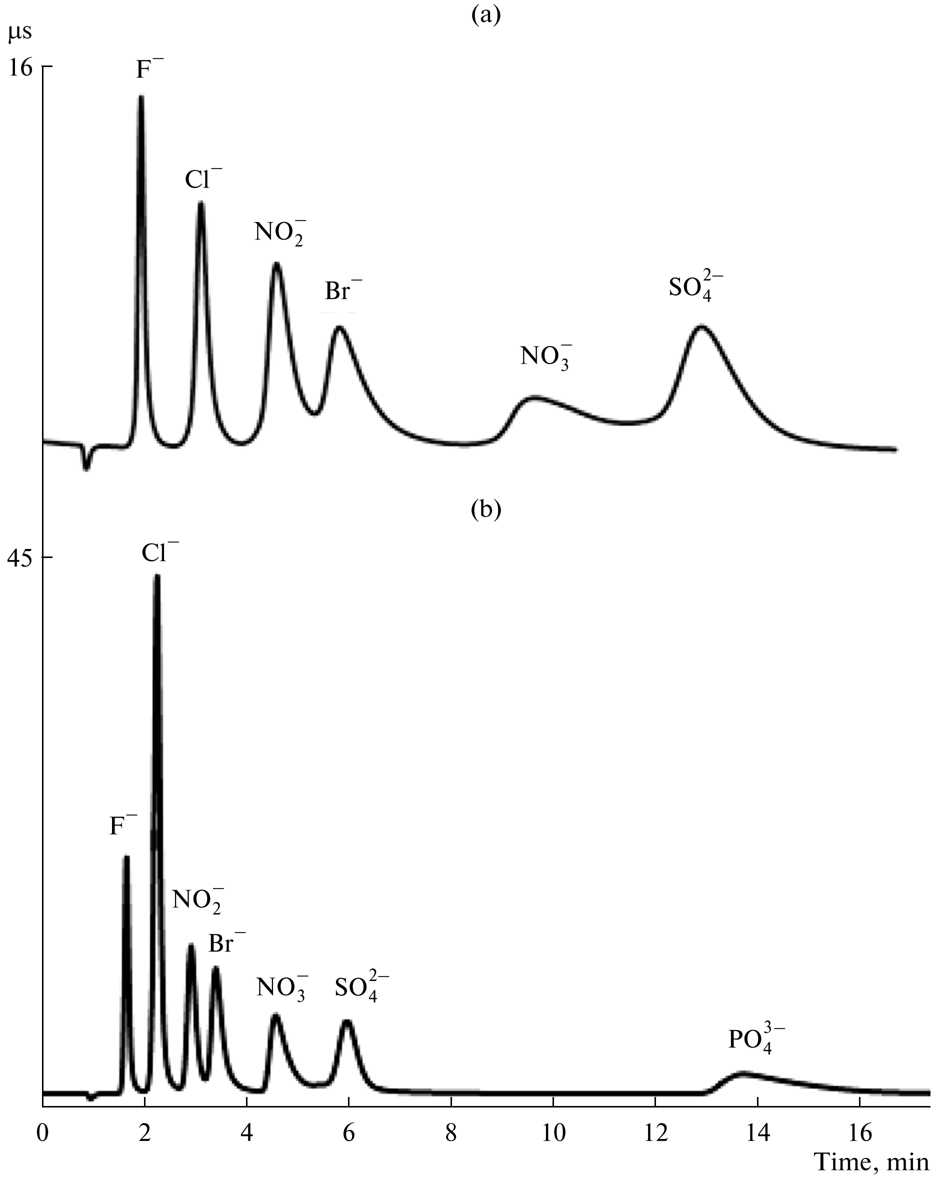

Fig. 5. Chromatograms of mixtures of inorganic anions in isocratic elution mode ($F = 0.5$ mL/min): a, sorbent B1 (eluent 7 mM KOH); b, sorbent B2 (eluent 10 mM KOH).

mation, are presented. As is seen from the equations, for all anions on the given anion exchangers, the slope of the curve corresponds to the ratio of their charge to the charge of the eluting hydroxide ion. Only the most polarizable nitrate ion, for which the slope on sorbent B1 with hydrophobic trimethylammonium FG does

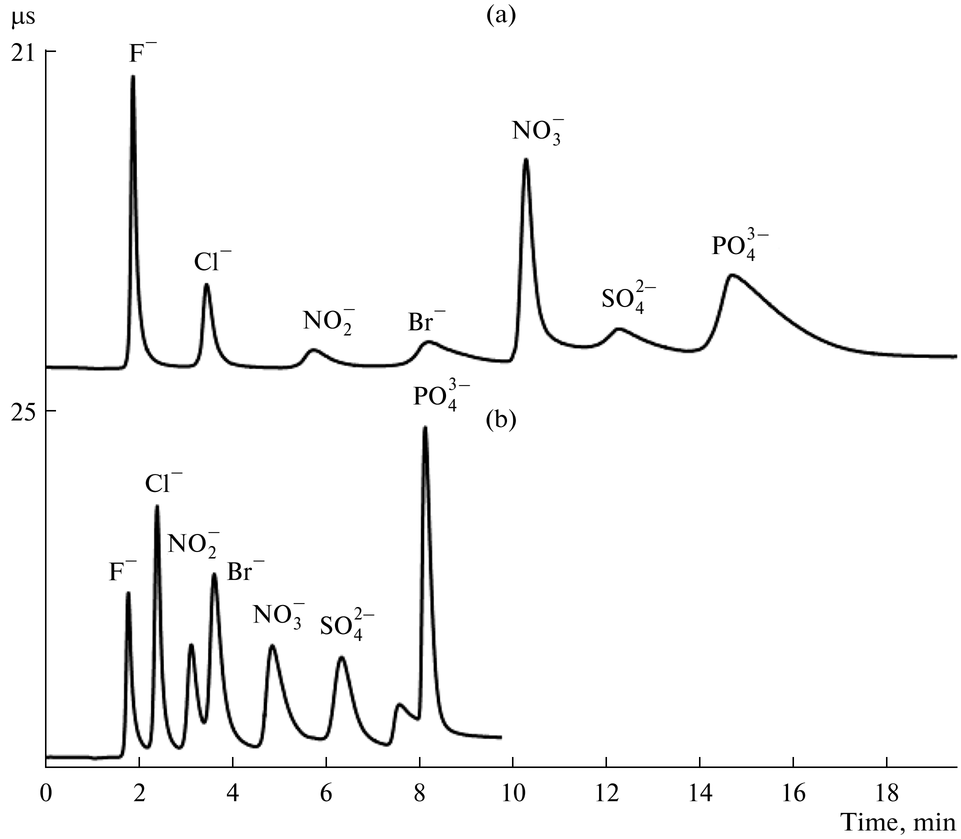

Fig. 6. Chromatograms of mixtures of inorganic anions in gradient elution mode ($F = 0.5$ mL/min): a, sorbent A2 (eluent 10 mM KOH: 0—8.5 min; 20 mM KOH: 8.6—20 min); b, sorbent B2 (eluent 7 mM KOH: 0—5.5 min; 20 mM KOH: 5.6—10 min).

not fall within the range 1.0 ± 0.1, is the exception. This fact indicates that the retention mechanism of this anion is not fully caused by ion exchange, and interaction with matrix has a certain contribution in its retention. Nevertheless, as was already mentioned, an increase in the hydrophilicity of an anion exchanger by

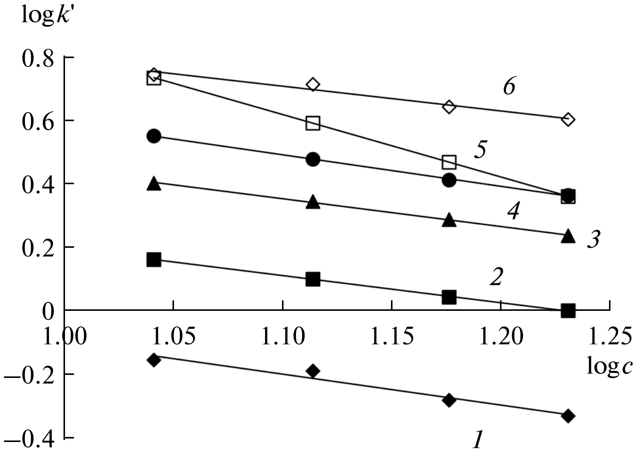

Fig. 7. Dependencies of the logarithm of capacity coefficients of the determined anions (*1*, F^-; *2*, Cl^-; *3*, NO_2^-; *4*, Br^-; *5*, SO_4^{2-}; *6*, NO_3^-) on logarithm of eluent concentration (KOH) for the B1 anion exchanger.

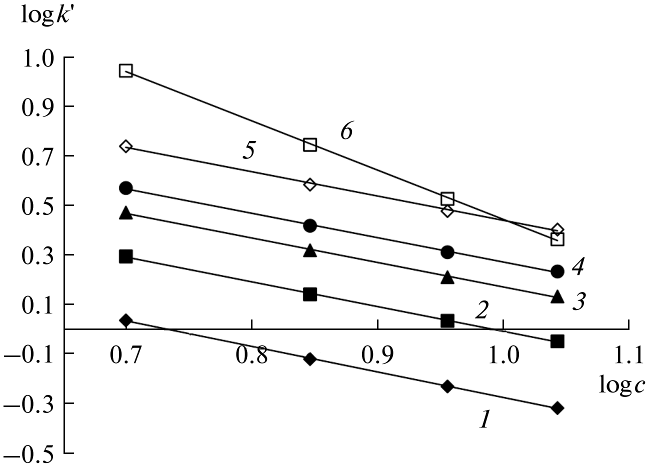

Fig. 8. Dependencies of logarithm of capacity coefficients of the determined anions (*1*, F^-; *2*, Cl^-; *3*, NO_2^-; *4*, Br^-; *5*, NO_3^-; *6*, SO_4^{2-}) on logarithm of eluent concentration (KOH) for the B2 anion exchanger.

Table 4. Equations of curves and coefficients of confidence of approximation of the dependencies $\log k'$–$\log c$ for sorbents B1 and B2 ($y - \log k'$, $x - \log c$)

Anion	Sorbent B1		Sorbent B2	
	equation	R^2	equation	R^2
F^-	$y = -0.9755x + 0.8732$	0.9598	$y = -1.0315x + 0.7574$	0.9997
Cl^-	$y = -0.8576x + 1.0537$	0.9993	$y = -1.0315x + 0.7574$	0.9997
NO_2^-	$y = -0.8759x + 1.3149$	0.9982	$y = -0.9904x + 1.1611$	0.9990
Br^-	$y = -0.9961x + 1.5853$	0.9990	$y = -0.984x + 1.2555$	0.9991
NO_3^-	$y = -0.7818x + 1.5649$	0.9690	$y = -0.9822x + 1.421$	0.9980
SO_4^{2-}	$y = -1.9711x + 2.7842$	1.0000	$y = -1.9877x + 2.4294$	0.9997

the introduction of hydrophilic radicals at the nitrogen atom, along with an increase of the spatial distance of FG from the aromatic basis of the sorbent, facilitates a significant decrease in the contribution of nonion-exchange interactions with the matrix in anion retention, which results in an increase in column efficiency.

Thus, as a result of this work, anion exchangers based on styrene–divinylbenzene with linear and branched structures of the ion exchange layer and two FGs of different hydrophilicities were obtained. It was shown that an increase in FG hydrophilicity and the creation of a branched ion exchange layer leads to an increase in the efficiency of the anion exchanger because of the elimination of the nonion-exchange interactions of anions with the matrix, which indicates the prospects of further development of the approach to modifying polymeric matrices involving the use of diglycidyl ethers and hydrophilic amines. The obtained anion exchanger with a branched structure of the ion exchange layer and hydrophilic FG is characterized by high selectivity and sufficiently high efficiency (40000 and 35000 theoretical plates/min in relation to nonpolarizable and polarizable ions respectively), which is comparable to the efficiency of some commercial sorbents.

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