

Effect of the Acylating Agent on the Selectivity of Anion-Exchange Resins and Separation Efficiency

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Received March 15, 2007

Abstract—Anion-exchange resins have been prepared by a two-step process that comprises the acylation of polystyrene/divinylbenzene (PS/DVB) with 50% crosslinking and subsequent amination with trimethylamine. The spacer arm between the quaternary ammonium functionality and the polymer backbone in these resins contains three, four, or five carbon atoms. An increase in the spacer arm improves the separation efficiency, affects the selectivity, and produces more symmetric peaks.

DOI: 10.3103/S002713140705015X

The chloromethylation of a polymer matrix followed by amine treatment is a classical route to crosslinked-polystyrene-based anion exchange resins. In the first study of chloromethylation, modifying was performed with chloromethyl ether in the presence of tin tetrachloride as a catalyst [1]. Chloromethyl ether has been included into the list of carcinogens [2], and its applications are limited. Methylene chloride and methylal have been proposed for use as alternative chloromethylating agents in the presence of acetic acid chloride and anhydrous zinc chloride [3], hydrochloric acid and paraformaldehyde [4], formaldehyde, thionyl chloride, chlorosulfonic acid [5], and others. However, chloromethylation has several weaknesses, including the probability of side reactions, the decreased mobility of the functionality because of the direct linkage to the polymer framework through a methylene group, and in some cases the hindered accessibility of the functionality to reagents and solvents. In addition, the chloromethylation of polystyrene/divinylbenzene (PS/DVB) resins is frequently accompanied by extra crosslinking [6, 7].

It was shown that the spatial separation of the functionality from the anion-exchange resin backbone offers a means for improving the chromatographic properties of the anion exchange resin, in particular its efficiency [8]. The alkylation of the polymer matrix with *n*-bromoalkene in the presence of trifluoromethanesulfonic acid as a catalyst, proposed in [9–11], is most widespread. The treatment of PS/DVB with *n*-bromoalkenes generates apolar alkyl chains (spacer arms) between the functionality and the anion-exchange resin backbone. A drawback of this method is the high cost of the reagents. It is more promising to employ acylation in the reaction of the benzene rings of the matrix with *n*-bromoacyl chlorides. This reaction generates chains that contain a polar carbonyl group [12]. Alkylated anion-exchange resins based on chlo-

romethylated PS/DVB matrices are well known in ion-exchange chromatography, whereas stationary phases containing a carbonyl group in the spacer arm between the functionality and the sorbent backbone are virtually unstudied.

Our goal in this work was to prepare anion-exchange resins for use in ion-exchange chromatography by means of Friedel–Crafts acylation using acylating agents with various numbers of carbon atoms and to compare the chromatographic properties of these anion-exchange resins.

EXPERIMENTAL

Instruments and Reagents

Experiments were carried out on a Staier (Akvilon) chromatograph equipped with a conductometric detector. Steel separation columns 4 × 50 mm in size packed using the suspension method under 250 bar were used. A column 4.6 × 150 mm packed with Dowex 50WX8 200–400 mesh cation-exchange resin in the H⁺ form (Supelco) was used to suppress the background signal.

The equipment used in the synthesis was as follows: thermostat (Mettmert), vacuum pump (Laboport), ultrasonic bath (Sapfir), and mechanical stirrer (Eurostar).

The matrix used to synthesize anion-exchange resins was 50 : 50 crosslinked PS/DVB, the grain size 3.3 ± 0.2 μm, the surface area 200 m²/g, the total pore volume 0.64 cm³/g, and the average pore diameter 6 nm (prepared in the Chromatography laboratory, Chemistry Department, Moscow State University).

The following reagents were used for modifying the matrix: dichloromethane, aluminum chloride (from Aldrich), tetrahydrofuran (Khimpromptorg), 3-chloropropionyl chloride (98.0%), 4-chlorobutyl chloride

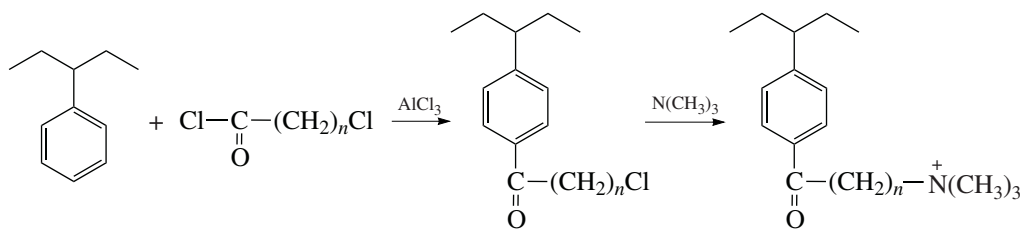


Fig. 1. Scheme of anion-exchange resin preparation.

(99.0%, Aldrich), 5-chlorovaleroyl chloride (97.0%+, Fluka), ethanol (analytical grade, Labtekh), acetonitrile (high purity grade for liquid chromatography, IREA 2000), and hydrochloric acid (Khimmed). The amination was performed with a 40% trimethylamine solution (Aldrich).

Analyte solutions and mobile phases were prepared from the following reagents: sodium carbonate (analytical grade), sodium hydrocarbonate (analytical grade), potassium sulfate (analytical grade), potassium nitrate (analytical grade), lithium chloride (analytical grade), potassium fluoride (reagent grade), and sodium dihydrogen phosphate (analytical grade) purchased from Khimmed or Labtekh.

Stock salt solutions with concentrations of 10 mmol/L were prepared from accurately weighed samples. Working solutions with lower concentrations were prepared by diluting the stock solutions. Eluents were prepared from 200-mM solutions of sodium carbonate and sodium hydrocarbonate. Distilled water was used to prepare all solutions.

Synthesis of Anion-Exchange Resins

Acylation. A 1-g aliquot of the matrix was transferred to a three-necked flask 100 mL in capacity, dichloromethane (12.5 mL) was added, and the mixture was allowed to stand for 2 h for swelling. After this, *n*-chloroacyl chloride (0.01 mol) was added. The reaction mixture was homogenized for 15 min at room temperature by stirring at 200 rpm. The acylation reaction was initiated by anhydrous aluminum chloride (0.137 g); the reaction mixture turned grayish brown. After 10 min, the reaction was stopped by adding tetrahydrofuran (50 mL). The product was filtered on a glass filter and washed with the following liquids: water–tetrahydrofuran (1 : 1), 2M HCl, water, and ethanol. After each washing stage, the reaction product was dried on a glass filter in vacuum created by a water-jet pump and then left on the filter over CaCl₂ in a desiccator until full drying.

Amination. At the second synthesis stage, a homogeneous suspension of a 1-g sample of the product obtained at the first stage in acetone (15 mL) was prepared; then, 40% aqueous solution of trimethylamine (15 mL) was added, and the mixture was stirred for 16 h at 70°C. After this time, 2 M HCl was added to stop

the reaction. The reaction product was filtered on a glass filter, washed under vacuo with two or three 2-M HCl portions (10 mL each), distilled water (until neutral pH), and ethanol. After this, the anion-exchange resin synthesized was left until full drying on a filter over CaCl₂ in a desiccator (Fig. 1).

Determination of the anion-exchange resin capacity. The ion-exchange capacity of sorbents was determined by converting them to sulfates in a dynamic mode. After the sorbents were completely converted from chlorides to sulfates with a 20 mM K₂SO₄ solution, the column was purged with distilled water to scavenge excess sulfate ions from the system. The SO₄²⁻ ions that were retained on the sorbent by the ion-exchange mechanism were eluted with 2 mM Na₂CO₃ solution. The eluate was collected to a graduated flask 100.0 mL in capacity and was chromatographed to determine the SO₄²⁻ concentration using a calibration curve. The time required for the full conversion of the sorbent from the Cl⁻ to SO₄²⁻ form or from the SO₄²⁻ to CO₃²⁻ form was judged from an abrupt change in electrical conductivity. Thus, the amount of sulfate (mmoles) required for converting the sorbent from the Cl⁻ to SO₄²⁻ form was determined in the eluate. The doubled sulfate ion concentration in the eluate was equal to the full exchange capacity of the anion-exchange resin. Dividing this value by the dry sorbent weight in the column, we found the specific exchange capacity. The results are displayed in Table 1.

RESULTS AND DISCUSSION

With the same amounts of *n*-chloroacyl chlorides, the anion exchange resins have different capacities, increasing from 3-chloropropionyl chloride to 5-chlorovaleroyl chloride. Apparently, lengthening of the spacer arm decreases the influence of the benzene ring, facilitating subsequent amination.

To study the ion-chromatographic behavior of anions on the sorbents, we chose the two-column ion-exchange chromatography version with a standard carbonate buffer solution as the eluent. Relative retention scales for inorganic anions on the anion-exchange res-

Table 1. Chromatographic parameters used to compare the anion-exchange resins synthesized

Separation column C ₃	Modifying agent: 3-chloropropionyl chloride; anion-exchange resin capacity: 0.032 mmol/L
Separation column C ₄	Modifying agent: 4-chlorobutyl chloride; anion-exchange resin capacity: 0.045 mmol/L
Separation column C ₅	Modifying agent: 5-chlorovaleroyl chloride; anion-exchange resin capacity: 0.080 mmol/L
Eluent	1.8 mM Na ₂ CO ₃ + 1.7 mM NaHCO ₃
Mobile-phase flow rate	0.8 mL/min
Detection method	Conductometry
Sample volume	50 μL
Anions to be determined	F ⁻ (2.5 mg/L), Cl ⁻ (5 mg/L), HPO ₄ ²⁻ (50 mg/L), NO ₃ ⁻ (25 mg/L), and SO ₄ ²⁻ (25 mg/L)

Table 2. Capacity factors for determined anions, peak asymmetry, and efficiencies of the anion-exchange resins studied (for the chromatographic parameters, see Table 1)

Anion	Sorbent C ₃			Sorbent C ₄			Sorbent C ₅		
	<i>k'</i>	<i>N</i> , TP/m	<i>A_s</i>	<i>k'</i>	<i>N</i> , TP/m	<i>A_s</i>	<i>k'</i>	<i>N</i> , TP/m	<i>A_s</i>
F ⁻	0.36	2300	0.66	0.48	4900	0.53	0.76	5400	0.58
Cl ⁻	0.51	5300	0.73	1.09	7000	1.04	2.31	8100	1.01
HPO ₄ ²⁻	0.93	7900	0.65	2.46	16800	0.93	6.76	55300	1.03
SO ₄ ²⁻	1.03	6500	0.52	3.10	16400	1.20	10.07	37400	1.04
NO ₃ ⁻	1.65	1600	*	5.04	1800	*	18.04	1600	*

* Not calculated.

ins studied are shown in Fig. 2. With the use of the carbonate eluent, all anion-exchange resins tested demonstrated an anomalous retention of the strongly polarized nitrate ion, which can be explained by π - π interactions with the aromatic nucleus of the ion-exchange resin.

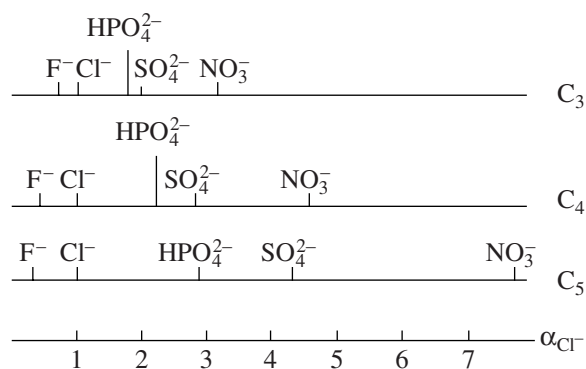
**Fig. 2.** Selectivity scales for anion-exchange resins C₃, C₄, and C₅. α is the selectivity factor (for the chromatographic parameters, see Table 1).

Figure 3 demonstrates chromatograms for the separation of five inorganic anions. One can see from this figure that the selectivity of the sorbents improves with increasing spacer arm length. On the one hand, this improvement can be because of the type of acylating agent; on the other hand, because of the exchange capacity increasing in the following order: 3-chloropropionyl chloride < 4-chlorobutyl chloride < 5-chlorovaleroyl chloride.

Figure 4 shows the log anion capacity of the anion-exchange resin as a function of the number of carbon atoms in the spacer arm of *n*-chloroacyl chloride. The plots are linear for all anions except for F⁻. The nonlinearity observed for F⁻ can be due to the exclusive retention of this ion on the suppressing column.

An increase in the distance between the functionality and the sorbent backbone generates narrower and more symmetric peaks. Table 2 displays the capacity factors for the test anions, the efficiencies of anion-exchange resins, and peak asymmetry coefficients. All anion-exchange resins are most efficient for phosphate ions. The highest efficiency (55 300 theoretical plates (TP)) was achieved for the anion-exchange resin modi-

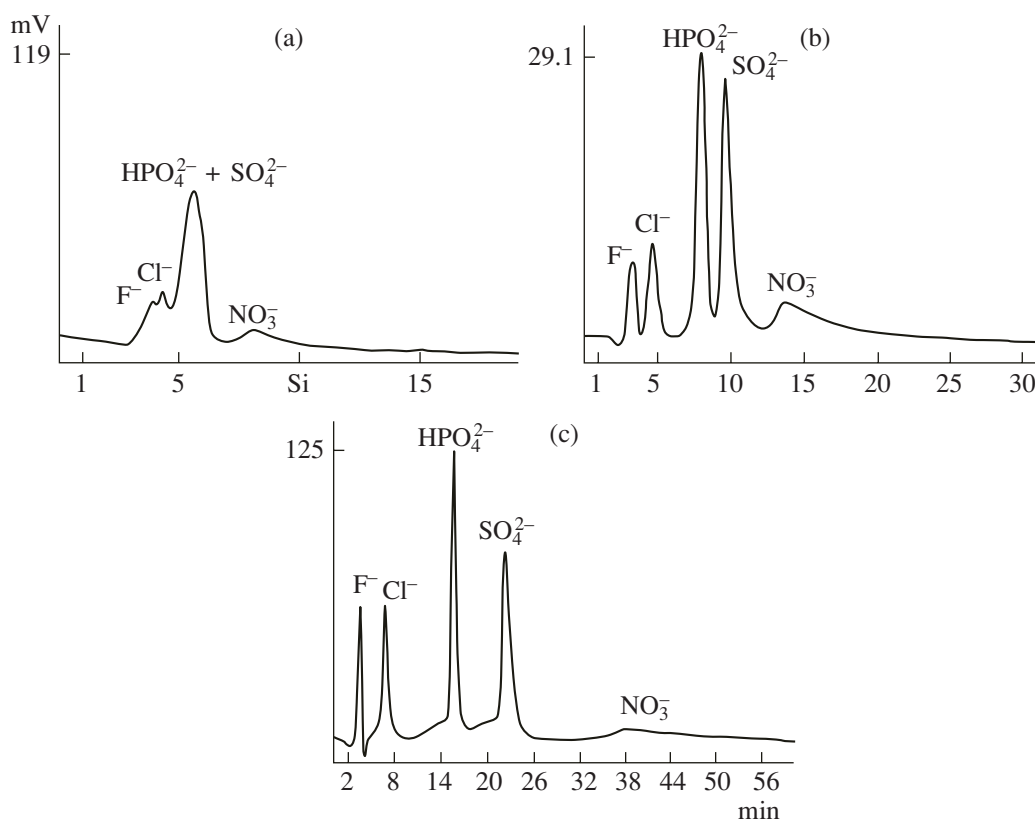


Fig. 3. Chromatograms of a model anion mixture under identical conditions on anion-exchange resins (a) C₃, (b) C₄, and (c) C₅ (for the chromatographic parameters, see Table 1).

fied with 5-chlorovaleroyl chloride. The peak asymmetry factor for this sorbent is near unity.

In summary, sorbents with a spacer arm between the functionality and polymer backbone containing three, four, or five carbon atoms have been synthesized on the basis of PS/DVB. The use of equal amounts of *n*-chloroacyl chlorides containing different numbers of carbon atoms in their chains affects the capacity and selectivity of the sorbents, peak asymmetry, and the efficiency of the chromatographic column; an increase in the number of carbon atoms in the spacer arm improves the specified parameters.

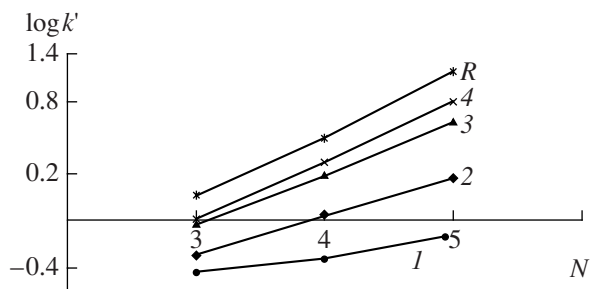


Fig. 4. Log plot of the capacity vs. number of carbon atoms in the spacer arm between the functionality and polymer backbone in the anion-exchange resin for (1) fluoride, (2) chloride, (3) phosphate, (4) sulfate, and (5) nitrate.

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