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Low-capacity latex-coated resins for anion chromatography

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ABSTRACT

Methods are described for coating latexes bearing a quaternary ammonium group onto spherical, non-porous polymeric resins. Exchange capacity of the coated resins is controlled by the amount of acetonitrile in the coating slurry and on the amount of latex in the slurry. A capacity range of 11–85 μequiv./g was obtained. Excellent chromatographic separations were obtained with columns packed with the coated resins. Sulfate is shown to elute before bromide and nitrate. As much as 40% methanol can be incorporated into the eluent without damaging the chromatographic column.

INTRODUCTION

Efficient anion-exchange resins for ion chromatography can be prepared by coating an unfunctionalized resin with a monomer or polymer containing a quaternary ammonium group. Cassidy and Elchuk [1] have developed both dynamic and permanent procedures for coating resins with long-chain quaternary ammonium compounds. DuVal and Fritz [2] demonstrated the successful use of permanently coated resin columns. Several other authors [3–5] have also used coated resins for ion chromatography.

As early as 1975 it was shown that efficient materials for anion chromatography can be prepared by coating resins that have been surface-sulfonated with a quaternized latex [6,7]. The positive charge of the latex is apparently attracted to the negatively charged sulfonate group on the resin surface.

Warth *et al.* [8] described the preparation and use of resins made by hydrophobically coating an anion-exchange latex onto unfunctionalized spherical resins. In the present study new latexes have been prepared and the method of coating has been altered in an attempt to obtain a more even coating and increase chromatographic efficiency. A latex that is only 54% quaternized was used to coat spherical polystrene beads. This material has very good chromatographic efficiency and can be used in conjunction with eluents containing up to 40% methanol.

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EXPERIMENTAL

Apparatus

The chromatographic systems consist of the following components. The first system consisted of a Milton-Roy mini-pump (Laboratory Data Control, Rivera Beach, FL, USA); a Rheodyne Model 7000 injection valve (Rainin, Woburn, MA, USA), equipped with a 10-μl sample loop; and a Milton-Roy pulse dampener (Laboratory Data Control) placed between the pump and the sample injector; a Spectroflow 783 (Kratos) variable-wavelength detector. This system was used for the indirect UV detection of the analytes. Various wavelengths were used and are noted in the text.

The second system consisted of an LKB 2150 high-performance liquid chromatography (HPLC) pump (Pharmacia), Wescan ICM II ion analyzer with conductivity detector (Alltech, CA, USA) and a Rheodyne Model 7125 injection valve fitted with a 10-μl sample loop.

A Shimadzu HPLC column packer (Phenomenex, CA, USA) was used to pack the column at a packing pressure ranging from 3000 to 6000 p.s.i. The columns used were 4.6 mm I.D., glass-lined, stainless-steel columns (Scientific Glass Engineering, Austin, TX, USA). Column lengths ranged from 5.0 to 15.0 cm in length and are noted in the text.

Resins

A 4.5-μm, spherical, non-porous, polystyrene resin with 10% divinyl benzene (DVB) cross-linking was prepared by expansion of monodisperse emulsion seed particles [9].

The latexes, which were 0.1 μm in diameter, were prepared by emulsifier-free terpolymerization of styrene, vinylbenzyl chloride and 5.5% DVB, followed by treatment with trimethylamine. The different levels of functionalization were obtained by varying the relative amounts of styrene and vinylbenzyl chloride.

Anion-exchange resins were produced by coating the 4.5-μm resin substrate with quaternized latex. Prior to the coating process, 10 ml of 4.5-μm resin was filtered in a medium, fritted-glass crucible, rinsed with 60 ml water and 30 ml of acetonitrile to remove adsorbed emulsifiers, and finally rinsed with deionized water. Then the rinsed resin was placed in a 100-ml beaker containing 45 ml of deionized water. In some cases acetonitrile was added at this point. The desired amount of latex was added dropwise with continuous magnetic stirring, and the total volume was brought to 50 ml by addition of water.

Coating experiments with varying percentages of acetonitrile were performed with 1 ml of latex suspension and 1 ml of polystyrene resin. Experiments on the effect of increasing amounts of latex suspension were performed in a slurry containing 1% (v/v) acetonitrile and 10 ml of polystyrene resin, with a final dilution to 25 ml. Resin exchange capacities were determined by a nitrate–sulfate displacement method. The coated resin [8] was packed using the upward packing method.

Reagents and solution

1,3,5-Benzenetricarboxylic acid (BTA) (97%, Aldrich) was purified by recrystallization from boiling, distilled, deionized water (Millipore). The precipitate was filtered by suction and washed. All other chemicals were of reagent grade or better, and were used without further purification. Distilled, deionized water was used throughout.

Eluents of phthalate and BTA were prepared by dissolving the acids in water and adjusting the pH with 0.1 *M* lithium hydroxide. Eluents were vacuum filtered through a 0.2-μm membrane filter and vacuum degassed. Stock solutions of sample anions were prepared from their sodium salts. Dicarboxylic acids were prepared from the acid and deprotonated with lithium hydroxide. Stock solutions of 1000 ppm were used and samples prepared by diluting aliquots of the stock solutions as necessary.

RESULTS AND DISCUSSION

Coating methods

Warth *et al.* [8] showed that efficient columns for anion chromatography could be produced by coating a spherical polystyrene resin with quaternized polymeric latex particles. They found that latexes 76% functionalized with quaternary ammonium groups adhered more tightly to the resin substrate and gave better separations than those that were 100% functionalized (one quaternary ammonium group per benzene ring).

It was felt that latexes with still lower percentages of funtionalization might provide even better coverage and ion-exchange efficiency. Accordingly, latexes were prepared that 76, 54, 47, 35 and 20% functionalized with quaternary ammonium groups. These were coated on to 4.5-μm non-porous polystyrene beads by the coating method used by Warth *et al.* [8]. The column efficiency of ion-chromatographic columns packed with 35 or 20% quaternized latex was very poor. Microscopic examination showed that these two latexes have a strong tendency to agglomerate and thereby give a very uneven coating. Some difficulty was also encountered with the 47% quaternized material. However, the 54% quaternized latex (like the 76%) showed much less tendency to agglomerate and was therefore used in all of the present research.

The first procedure used to prepare coated resins involved filtering the 4.5-μm resin substrate and washing with water before coating with the 54% latex. While this produced resins that gave good chromatographic separations, the resin capacity was unpredictable. Variations in capacity were caused by the presence of adsorbed emulsifiers that competed with the latex for adsorption sites on the resin surface. This situation was corrected by first washing the filtered resin substrate with acetonitrile and then with water before the coating step. The rinsed resin temporarily agglomerated during the coating step, but the aggregates dispersed as the substrate became coated with the quaternized latex. Continuous stirring of the mixing slurry also facilitated breaking up the aggregates. The resulting anion-exchange resin produced excellent separations. It was also possible to alter the capacity in a predictable manner.

Previous work involving latex that had 76 and 100% functionalization demonstrated that the capacity of the coated resin was dependent on the length of time the slurry was mixed, on the concentration of NaCl and on the amount of functionalized latex present in the slurry [8]. In each case, capacity increased as one or more of these three parameters increased. In the present work with 54% functionalized latex, it was found that the final resin capacity was independent of the concentration of NaCl or the length of time the latex and substrate were mixed together. For example, after 1, 2 and 4 h of continuous mixing, the resin had a capacity of 27.3, 26.7 and 27.7 μequiv./g, respectively. This is probably due to the more hydrophobic nature of this latex which causes the latex to reach equilibrium quickly between the resin and the aqueous slurry.

The presence of sodium chloride in the aqueous slurry actually had a deleterious effect when 54% functionalized latex was used. Increasing the ionic strength of the slurry resulted in formation of latex aggreates that could be observed with an optical microscope (21 ×). This produced an unevenly coated resin and inefficient chromatographic columns. By having 1% (v/v) acetonitrile in the slurry, the problem of latex aggregation was alleviated and no aggregates could be seen with the microscope. A marked improvement in column efficiency was observed when this resin was tested chromatographically. Efficiencies as high as 19 500 theoretical plates per meter were obtained at a flow-rate of 1 ml/min. Increasing the percentage of acetonitrile in the slurry to greater than 1% did not further improve the chromatographic efficiency when the slurry contained a 1:10 latex-to-substrate ratio.

Capacity

The capacity of the coated resin can be controlled by the percentage of acetonitrile present in the slurry and the amount of latex used. Fig. 1 shows that, as expected, the capacity decreases as the percentage of acetonitrile increases. As the slurry becomes more hydrophobic, the latex is less readily adsorbed onto the hydrophobic substrate. It is interesting to note that while previous work indicated that

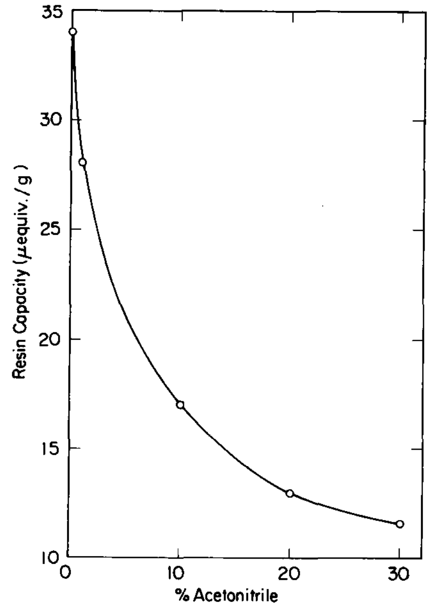


Fig. 1. Relationship between resin capacity (μequiv./g) and percent acetonitrile present in slurry. Each slurry contained 1 ml of latex suspension and 1 ml of washed polystyrene substrate, diluted to 25 ml and stirred for 1 h.

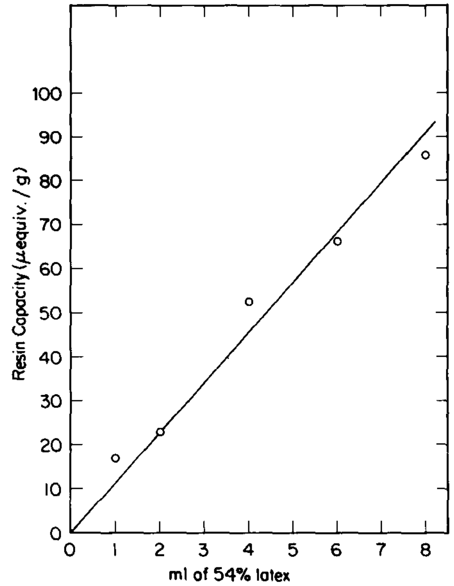


Fig. 2. Relationship between resin capacity and volume of latex added to slurry. Each slurry contained 10 ml of polystyrene substrate and 1% (v/v) acetonitrile. Other conditions as in Fig. 1.

organic modifiers washed the higher-functionalized latexes off the substrate, anion-exchange resins were able to be prepared in the presence of acetonitrile using the 54% functionalized latex.

Fig. 2 shows a nearly linear increase in capacity as the volume of latex used to coat the substrate was increased. Since this latex is more hydrophobic, a heavier coating was possible than with previous latexes. By varying the percentage of acetonitrile and the volume of latex used in the slurry, the capacity can be varied from 11.5 to 85 μequiv./g.

Selectivity

Fig. 3 shows the separation of seven common anions in less than 7 min. The column is 50 × 4.6 mm I.D. Even though a short column was used, a nearly baseline separation was possible in a short analysis time. The eluent was 0.8 m*M* dilithium phthalate at pH 9.50. It is interesting to note that SO_4^{2-} and $C_2O_4^{2-}$ elute before Br^-. This is unexpected, since resins made with 76% functionalized latex of identical capacity did not show this elution order using a phthalate eluent [10].

Effect of methanol

The effect of adding methanol to the eluent was studied next. The presence of methanol affects some anions more than others, as illustrated by the retention times in Table I. There is a substantial change in the retention times of sulfate, bromide and nitrate, while the retention time sof chloride and nitrite are less affected.

A commercial column (Wescan 269-029) was also used to investigate the effect of methanol on the retention times of these anions. The retention times of Cl^-, NO_2^-,

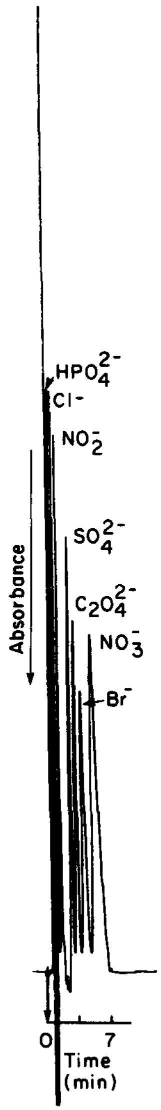


Fig. 3. Separation of 5 ppm HPO_4^{2-}, 2.5 ppm Cl^-, 5 ppm NO_2^-, 10 ppm SO_4^{2-}, 10 ppm $C_2O_4^{2-}$, 20 ppm Br^- and 30 ppm NO_3^- on a 5.0 cm × 4.6 mm I.D. column (capacity = 27 μequiv./g). Eluent, 0.8 m*M* dilithium phthalate at pH 9.50; flow-rate, 1 ml/min; wavelength λ = 250 nm; 0.025 a.u.f.s.

Br^- and NO_3^- were unaffected and SO_4^{2-} increased only slightly. The ability to alter selectivity by using an organic modifier in the eluent provides a novel dimension to latex-coated resins.

The stability of 54% functionalized latex in the presence of methanol was also investigated. After using 40% methanol in the eluent, aqueous phthalate was again used. The retention times of the anions and the elution order were essentially the same as before the use of methanol. We do not claim that 40% methanol can be used

TABLE I

EFFECT OF METHANOL AS ELUENT MODIFIER ON THE ADJUSTED RETENTION TIMES OF FIVE COMMON ANIONS

CH_3OH in eluent (%)	Average adjusted retention time (min, n = 3)				
	Cl^-	NO_2^-	SO_4^{2-}	Br^-	NO_3^-
0	0.62	0.99	2.93	3.64	4.60
10	0.67	1.02	3.82	3.82	4.72
20	0.66	0.96	4.53	3.57	4.53
30	0.64	0.86	5.48	3.20	3.81
40	0.61	0.76	6.47	2.78	3.22

indefinitely, although use for 8 h had no effect on analyte retention times. Fig. 4 shows a very nice separation of eight anions after using 40% methanol in the eluent. The two dicarboxylic acids were not resolved.

Applications

The analysis of dicarboxylic acids is important in industries such as the wine

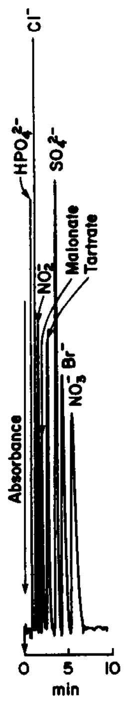
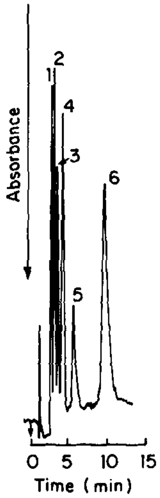


Fig. 4. Separation of 10 ppm HPO_4^{2-}, 5 ppm Cl^-, 5 ppm NO_2^-, 10 ppm malonate, 20 ppm tartrate, 25 ppm SO_4^{2-}, 30 ppm Br^- and 30 ppm NO_3^-, after 40% methanol was used as eluent modifier. Eluent, 0.5 mM dilithium phthalate at pH 8.25; flow-rate, 1 ml/min; column, 10 cm × 4.6 mm I.D. with a capacity of 35 μequiv./g, λ = 270 nm; 0.025 a.u.f.s.



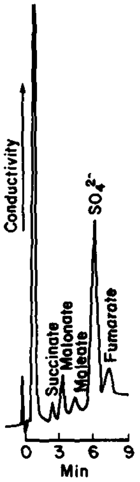
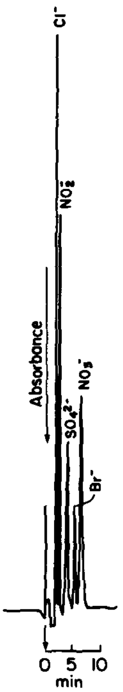


Fig. 5. Separation of 10 ppm glutarate, 10 ppm succinate, 10 ppm malate, 10 ppm malonate, 5 ppm tartrate and 20 ppm oxalate using indirect UV detection on a 10 cm × 4.6 mm I.D. column (capacity = 28 μequiv./g). Eluent, 0.2 m*M* dilithium phthalate at pH 8.40; λ = 245 nm; 0.025 a.u.f.s.

Fig. 6. Separation of 10 ppm each succinate, malonate, maleate, sulfate and fumarate using conductivity detection (1 μS f.s.). Eluent, 0.25 m*M* dilithium phthalate at pH 8.50, column same as in Fig. 5.



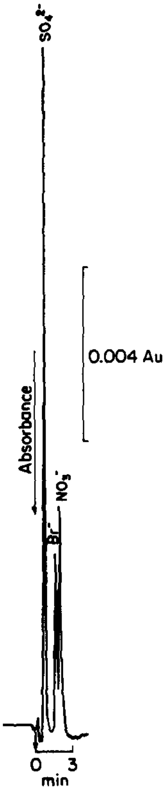


Fig. 7. Separation of 10 ppm Cl^-, 10 ppm NO_2^-, 10 ppm SO_4^{2-}, 10 ppm Br^- and 20 ppm NO_3^- on a 5 cm × 4.6 mm I.D. column (capacity = 27 μequiv./g). Eluent, 0.05 m*M* BTA at pH 4.3, flow-rate, 1 ml/min, λ = 250 nm; 0.025 a.u.f.s.

Fig. 8. Rapid separation of 5 ppm each SO_4^{2-}, Br^- and NO_3^- on a 5.0 cm × 4.6 mm I.D. column (capacity = 15 μequiv./g). Eluent, 0.05 m*M* BTA at pH = 4.6; flow-rate 1 ml/min; λ = 240 nm; 0.025 a.u.f.s.

industry. Fig. 5 shows a nice separation of six dicarboxylic acids in 10 min. As the alkyl chain length of the dicarboxylic acids increases, the retention times of the acids decrease. As the carboxylic acid moieties are farther apart, the molecule behaves chromatographically more like a monovalent anion.

Indirect UV detection is the detection method of choice for analyzing dicarboxylic acids. Fig. 6 shows a separation of 10-ppm each succinate, malonate, maleate, sulfate and fumarate, using 0.25 m*M* dilithium phthalate at pH 8.5 as the eluent with conductivity detection. A comparison between Fig. 5 and Fig. 6 demonstrates that indirect UV detection is much more sensitive.

Very low exchange capacities can be obtained readily with latex-coated resins. This makes it possible to obtain excellent sensitivity in the analysis of low concentrations of anions. The effect of capacity on sensitivity is illustrated by the chromatograms in Figs. 7 and 8. The chromatographic conditions are almost the same except that the resin capacity is 27 μequiv./g in Fig. 7 and 15 μequiv./g in Fig. 8. The retention times of sulfate, bromide and nitrate are all smaller on the lower capacity column (Fig. 8) and the peak heights per 1 ppm of anion are 4–8 times larger on the column of lower capacity. Excellent calibration curves were also obtained. For example, linear calibration curves were obtained from 0.5 to 50 ppm chloride and sulfate, and from 1.5 to 75 ppm nitrate with correlation coefficients of 0.9997 or better.

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