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LOW-CAPACITY QUATERNARY PHOSPHONIUM RESINS FOR ANION CHROMATOGRAPHY

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SUMMARY

Trimethylammonium, tributylammonium and tributylphosphonium anion-exchange resins were synthesized and used for single-column ion chromatography. The three resins were prepared using a 7–12-μm polystyrene–divinylbenzene resin and are all of a similar, low capacity. The selectivity of these resins for mono- and divalent anions was evaluated and unique anion separations are presented.

INTRODUCTION

Since the introduction of suppressed ion chromatography (SIC) in 1975[1] and single-column ion chromatography (SCIC) in 1979[2], several types of ion exchangers have been used to separate anions. The original work in SIC by Small and Stevens[3] used agglomerated, pellicular resins of a low exchange capacity. Chemically-bonded polymeric resins of an even lower capacity were used by Gjerde *et al.*[2] in SCIC. More recently, statically- or dynamically-coated resins have become popular in anion chromatography, largely because of ease of column preparation[4–6].

Most stationary phases used in anion chromatography are "strong-base" quaternary ammonium resins. The resins most often used are referred to as Type I (benzyltrimethylammonium cation) and Type II (one methyl group replaced by a hydroxyethyl group) resins. A few other types of strong-base resins have also been used in anion chromatography. For example, Barron and Fritz[7,8] synthesized a series of quaternary ammonium resins with varying R group lengths that were used to study the effect of functional group structure on anion selectivity.

Although quaternary ammonium resins have been used extensively as stationary phases[9–11], quaternary phosphonium resins have also been synthesized[12,13]. Most recent work shows that quaternary phosphonium resins have been used extensively as phase-transfer catalysts[14,15]. In many cases, the quaternary phosphonium phase-transfer catalysts were more active catalytically than the analogous quaternary ammonium catalysts[16–18].

To our knowledge, low-capacity quaternary phosphonium ion-exchange resins have never been used in single-column ion chromatography.

There are two major differences (possible advantages) of a tributylphosphoni-

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um (TBP) resin compared with a tributylammonium (TBA) resin: (1) TBP is more reactive than TBA and resins of higher exchange capacity can be prepared, (2) the TBP resin has a considerably higher affinity for nitrate, compared to sulfate, than the TBA resin. This property is being used in other work on the selective removal of nitrate from water supplies. The goal of this work is to synthesize a quaternary phosphonium resin of a low capacity which is suitable for anion chromatography. The preparation, performance, and selectivity of this resin in anion chromatography are then evaluated and compared to that of two different quaternary ammonium ion-exchange resins.

EXPERIMENTAL

Materials and equipment

The 7–12-μm, spherical polystyrene–divinylbenzene resin (PS–DVB) was obtained by courtesy of Dr. Douglas Gjerde at Benson Co. (Reno, NV, U.S.A.). The 25% trimethylamine (in methanol) and tributylamine were obtained from Aldrich (Milwaukee, WI, U.S.A.). The tributylphosphine was obtained from Aldrich or Sigma (St. Louis, MO, U.S.A.). The paraformaldehyde and concentrated hydrochloric acid used for the chloromethylation reactions were obtained from Mallinckrodt (Paris, KT, U.S.A.). The solvents used for rinsing resin were of reagent grade and were obtained from a number of sources. All reagents were used as received.

Ion chromatography was carried out on one of two instruments, both built from similar components. An LKB 2150 high-performance liquid chromatography (HPLC) pump (Pharmacia LKB Biotechnology, Piscataway, NJ, U.S.A.) or a Milton Roy Mini-pump manufactured by Laboratory Data Control (Riviera Beach, FL, U.S.A.) equipped with a high-pressure pulse dampener provided eluent flow. Rheodyne (Berkeley, CA, U.S.A.) Model 7010 injection valves fitted with 50-μl sample loops were used for sample introduction. The resins were packed in glass-lined stainless-steel columns (250 × 2.0 mm I.D.) that were obtained from Scientific Glass Engineering (Austin, TX, U.S.A.). An Eldex (Menlo Park, CA, U.S.A.) column heater or home-made insulation was used to insulate the column and prevent baseline drift. Detectors used were Model 213A conductivity detectors manufactured by Wescan Instruments (Santa Clara, CA, U.S.A.). Strip-chart recorders manufactured by Curken Scientific (Danbury, CT, U.S.A.) were used to record chromatograms.

Procedures

Chemically-bonded resins were prepared using a two-step procedure. First, a formaldehyde–hydrochloric acid procedure[19] was used to chloromethylate the resin. Standard conditions for the chloromethylation reactions employed 1.0 g of resin and 2.2 *M* paraformaldehyde in 25-ml of 10 or 12 *M* hydrochloric acid at room temperature. Then, 40 ml of a 2.0 *M* or greater solution of trimethylamine (TMA), tributylamine (TBA) or tributylphosphine (TBP) in methanol or 1,2-dichloropropane (1,2-DCP) was reacted with the chloromethylated resin at 60–70°C for at least 24 h to obtain quaternary ammonium or phosphonium resins. The amination and phosphination procedures are similar to those in previously-published works[18,19].

The control quaternization experiment was performed by first chloromethylating 1.0 g of resin using 2.2 *M* paraformaldehyde in 12 *M* hydrochloric acid for 18.5

min. The chloromethylated batch of resin was then divided into equal parts and aminated or phosphinated using exactly 2 *M* concentrations of the reagent in 40 ml of either methanol or 1,2-DCP. After amination, the resin was filtered and washed thoroughly with 2.0 *M* hydrochloric acid, water, 2-propanol, water and methanol. The functionalized resin was then air dried.

The strong-base ion-exchange capacities of the resins were determined by rinsing a weighed portion of resin with methanol, water, 0.5 *M* potassium nitrate and then again with water to remove any excess nitrate. The resin was then transferred to a gravity column and the bound nitrate was eluted with 0.005 *M* potassium sulfate. The collected nitrate was then determined spectrophotometrically at 225 nm.

All solutions were made up in distilled, deionized water and were prepared from reagent grade salts. Eluents were prepared by dissolving the acid in distilled, deionized water and, if necessary, adjusting the pH by adding sodium hydroxide. The eluents were then filtered through a 0.2-μm membrane filter after which a vacuum was applied while stirring to remove dissolved gases.

Columns were packed using an upward packing, stirred slurry technique with 40% ethylene glycol and 1% sodium chloride in water as the packing solvent. The packing pressure was approximately 4500 p.s.i. The instrument used to pack the columns was a Shandon HPLC packing pump (Phenomenex, Rancho Palos Verdes, CA, U.S.A.).

RESULTS AND DISCUSSION

Preparation of resins

The purpose of this study was to evaluate and compare the selectivity and performance of low-capacity quaternary phosphonium and ammonium resins in anion chromatography. Three types of resins were prepared; the structures are shown in Fig. 1. All factors other than the structure of the functional group were held constant. For example, the resins were all prepared from the same resin lot and were synthesized to obtain similar exchange capacities so that identical elution conditions could be used.

The anion-exchange resins were prepared by chloromethylating a cross-linked polystyrene resin, followed by reaction with a tertiary amine (TMA or TBA) or a tertiary phosphine (TBP). It became apparent immediately that the reactivities of the

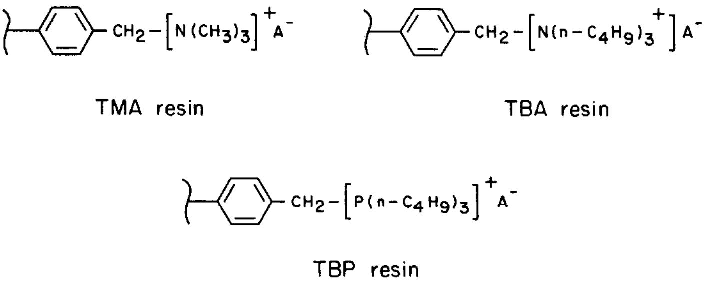


Fig. 1. Structures of the three resins synthesized and compared chromatographically: trimethylammonium resin (TMA), tributylammonium resin (TBA) and tributylphosphonium resin (TBP).

TABLE I

PREPARATION OF CHROMATOGRAPHIC RESINS

Reaction conditions are listed in the Experimental section.

Resin	*Designation*	*Chloromethylation time (min)*	*HCl (M)*	*Amination solvent*	*Capacity (μequiv./g)*
Trimethylammonium	TMA	2, 2.6, 2.5[a]	10	Methanol	90.2
Tributylammonium	TBA	125	12	Methanol	93.3
Tributylphosphonium	TBP	18.5	12	1,2-DCP	96.9

[a] Three separate chloromethylation and amination reactions were used to obtain a total TMA capacity of 90.2 μequiv./g.

TMA, TBA and TBP were greatly different. The following exchange capacities were obtained after performing a control experiment and reacting portions of the same chlormethylated resin with an amine or phosphine at 60–70°C for 24 h: TMA, 219.1 μequiv./g; TBA, 53.1 μequiv./g; TBP, 93.5 μequiv./g.

It was possible, however, to prepare resins of almost the same exchange capacity by varying the extent of chloromethylation. The major synthetic conditions and properties of the quaternary ammonium and phosphonium resins used in this study are summarized in Table I. Note that the times used for chloromethylation were varied considerably to compensate for the differences in reactivity of the amines and phosphine.

Evaluation of resin selectivity

Although the exchange capacities of the three resins in Table I are similar, there is a considerable difference in the amounts of unreacted chloromethyl groups. The

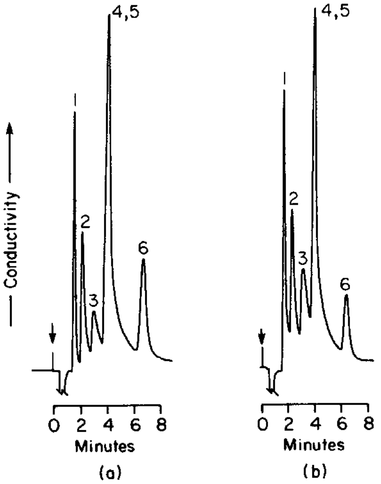


Fig. 2. Separation on TMA resins of (1) chloride, (2) nitrite, (3) bromide, (4) sulfate, (5) nitrate and (6) thiosulfate using 1 m*M* sodium phthalate at pH 6.5 as the eluent at a flow-rate of 0.75 ml/min. Anion concentrations were 6–50 ppm each. (a) TMA resin with a capacity of 70.1 μequiv./g. (b) TMA resin with a capacity of 70.1 μequiv./g and 121 μequiv./g excess chloromethyl groups.

presence of excess chloromethyl groups has been noted previously[20], but the effect of these groups on anion selectivity has not been studied.

Fig. 2 shows chromatograms of identical sample mixtures obtained on the same batch of TMA resin. The separation shown in Fig. 2a was obtained with a resin that was first chloromethylated and then aminated using TMA to obtain an exchange capacity of 70.1 μequiv./g. This column was then unpacked, chloromethylated again, repacked and tested. Fig. 2b shows a separation using the TMA resin (70.1 μequiv./g with excess chloromethyl groups. Identical eluent conditions and sample mixtures were used in both cases. A portion of the resin was again aminated with TMA and a capacity of 191 μequiv./g was obtained. Because of the similarity of these chromatograms, it can be concluded that the presence of excess chloromethyl groups (at a level of 121 μequiv./g) on an anion-exchange resin has virtually no effect on the selectivity of the anions tested in this study.

Columns were packed with TMA, TBA and TBP resins and retention times for a number of anions were measured using identical elution conditions for each column. Relative retention times were then calculated by dividing the adjusted retention time of each anion by the adjusted retention time of chloride. This corrects for the small differences in resin capacity and for any other slight differences in elution conditions.

The relative retention times of various anions are given in Table II using two different eluents. Many of the anions tested show very little change in relative retention on the three columns. However, large polarizable anions, such as bromide, nitrate and iodide, show higher relative retention times on TBA compared to TMA and still higher relative retention times on the TBP column. Chlorate shows almost the same retention times on the quaternary ammonium columns but a distinctly higher relative retention time on the quaternary phosphonium column.

The effect of larger R groups in quaternary ammonium resins on the retention of poorly hydrated anions like bromide, nitrate and iodide has been noted previously[7]. This effect has been attributed to stronger ion pairing that results from disruption of the water structure by these anions and from a tightening of the water structure surrounding the ion pair caused by the larger R groups. These effects appear to be enhanced further by going from a quaternary ammonium to a quaternary phosphonium resin. The phosphonium group is larger and more hydrophobic than the ammonium exchange site. This causes a greater tightening of the water structure around the ion pair and results in longer relative retention times for ions like bromide, nitrate and iodide.

Eluent pH

Chromatograms of a number of anions were compared on TBA and TBP resin columns using 1.5 m*M* sodium phthalate at several pH values. Results for a few of the anions are shown in Figs. 3 and 4. At higher eluent pH values the relative retention times of divalent anions decrease, as expected, because the eluent is present primarily as the 2− anion. However, the relative retention times of monovalent anions increase as the eluent pH becomes higher. This effect is especially pronounced for nitrate and chlorate.

The longer retention of anions such as nitrate and chlorate at higher eluent pH values is rather puzzling, because a 2− eluent anion should elute monovalent sample

TABLE II

SELECTIVITY DATA FOR QUATERNARY AMMONIUM AND PHOSPHONIUM ION-EXCHANGE RESINS

Conditions: the TMA column is a trimethylammonium resin with a capacity of 90.2 μequiv./g. The TBA column is a tributylammonium resin with a capacity of 93.3. μequiv./g. The TBP column is a tributylphosphonium resin with a capacity of 96.9 μequiv./g. All flow-rates were 0.75 ml/min and detection was by conductivity.

Anion	$t'_R/t'_{R,chloride}$					
	30 mM nicotinic acid			*2.2 mM sodium phthalate, pH 6.0*		
	TMA column	*TBA column*	*TBP column*	*TMA column*	*TBA column*	*TBP column*
Acetate	–	–	–	–	0.73	0.67
Glycolate	0.22		0.20	–	–	–
Lactate	0.30	0.25	0.25	–	–	–
Formate	0.34	0.33	0.29	–	–	–
Fluoride	0.39	0.35	0.32	–	–	0.50
Dihydrogenphosphate	0.46	0.44	0.43	0.63	0.71	0.62
Iodate	0.50	0.47	0.44	–	–	0.49
Azide	0.54	0.49	0.50	–	–	–
Methylsulfonate	0.95	0.89	0.86	0.95	0.98	0.94
Propionate	0.96	0.42	0.46	–	–	–
Chloride	1.00	1.00	1.00	1.00	1.00	1.00
Bromate	1.51	1.22	1.26	1.25	1.15	1.22
Ethylsulfonate	1.61	1.18	1.20	1.49	1.33	1.35
Nitrite	1.33	1.34	1.46	1.49	1.59	1.60
Bromide	2.38	2.65	3.02	1.91	2.30	2.69
Malonate	–	–	–	2.09	2.72	2.53
Sulfate	–	–	–	2.09	2.42	2.32
Nitrate	3.08	4.53	5.20	2.49	3.68	4.31
Thiosulfate	–	–	–	3.57	3.77	3.66
Chlorate	–	–	–	4.32	4.34	5.28
Propylsulfonate	–	–	–	4.92	3.20	3.38
Iodide	–	–	–	9.60	17.88	29.08
t'_R for Cl^- (min)	6.95	12.39	11.63	0.85	1.11	1.19

anions more quickly than a 1 – eluent anion. One possible explanation is that more phthalate is adsorbed on the resin surface at pH 4.5 than at pH 6.5[21]. This adsorbed phthalate could partially relax the water structure surrounding the exchange site and lessen the effects of water-induced ion pairing on nitrate and chlorate. At pH 6.5, much less phthalate is adsorbed and the stronger water-induced ion pairing results in longer retention times for anions like nitrate and chlorate.

Chromatographic separations

Fig. 5 shows chromatograms comparing separations of several inorganic anions on all three columns. The eluent used was 1.5 m*M* sodium phthalate (pH 6.5) operated at a flow-rate of 0.75 ml/min. Using these conditions, the TBP separation shows much greater resolution of the peaks separated. This results primarily from the

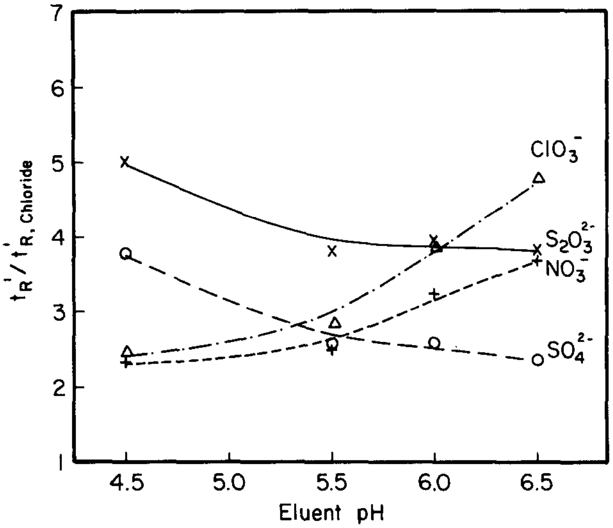


Fig. 3. Relative retentions *versus* eluent pH using the TBA column (93.3 μequiv./g) and a 1.5 m*M* sodium phthalate eluent. Detection was by conductivity.

greater retention of the monovalent bromide and nitrate anions obtained on TBP column.

Figs. 6 and 7 shows additional examples of separations obtained with the TBP column. Fig. 6 shows a separation of chloride and several divalent anions (sulfate, oxalate, tungstate, thiosulfate and chromate). Conductivity detection is used and the

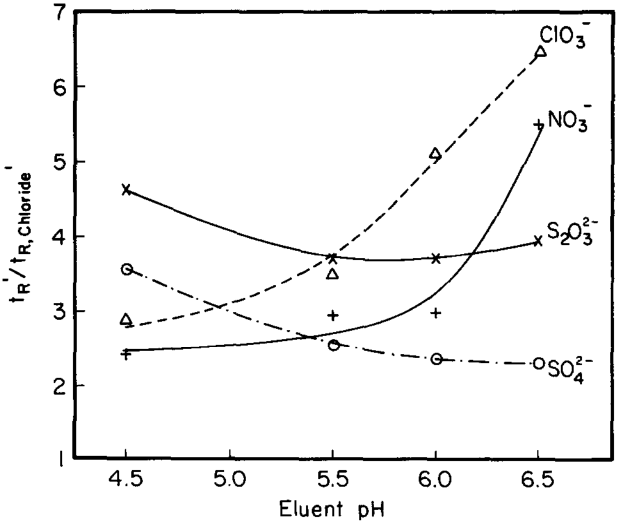


Fig. 4. Relative retentions *versus* eluent pH using the TBP column (96.9 μequiv./g) and a 1.5 m*M* sodium phthalate eluent. Detection was by conductivity.

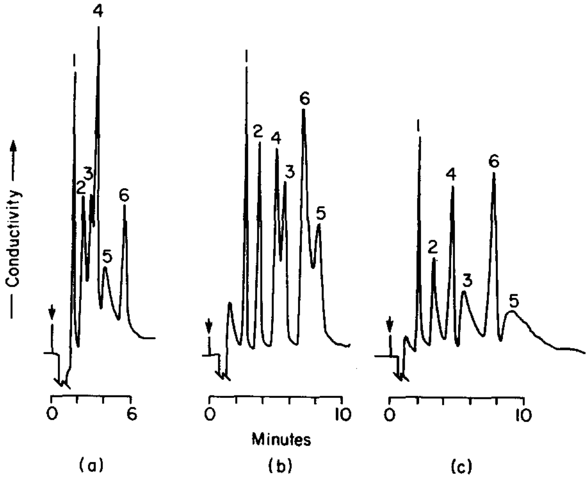
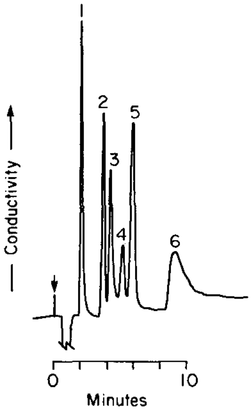


Fig. 5. Separation of common inorganic anions on TMA (a), TBA (b) and TBP (c) columns. Resin capacities are 90.2, 93.3 and 96.9 μequiv./g, respectively. The eluent was 1.5 m*M* sodium phthalate (pH 6.5) at a flow-rate of 0.75 ml/min. Detection was by conductivity. Anions are (1) chloride, (2) nitrite, (3) bromide, (4) sulfate, (5) nitrate and (6) thiosulfate at concentration levels of 6–30 ppm each anion.



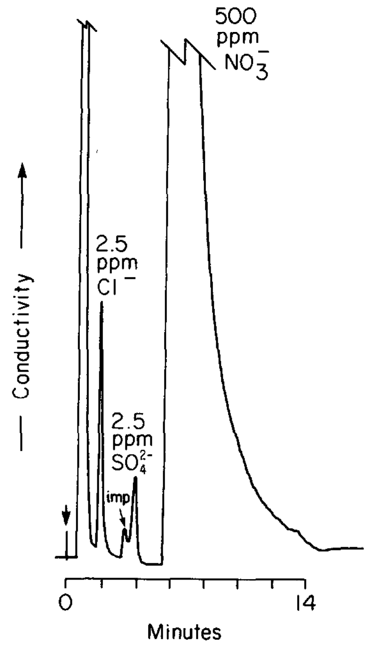


Fig. 6. Separation of chloride and late-eluting anions on the TBP column (96.9 μequiv./g). The eluent was 2.2 m*M* sodium phthalate (pH 6.5) at a flow-rate of 0.75 ml/min. Detection was by conductivity. Anions are (1) 6 ppm chloride, (2) 7.5 ppm sulfate, (3) 10 ppm oxalate, (4) 20 ppm tungstate, (5) 12.5 ppm thiosulfate and (6) 40 ppm chromate

Fig. 7. Separation of low levels of chloride and sulfate in the presence of large amounts of nitrate using the TBP column (96.9 μequiv./g). Separation conditions are listed in Fig. 7.

eluent is 2.2 m*M* sodium phthalate at pH 6.5. The higher capacity of this column and high pH of this eluent allow chloride and the divalent anions that are normally late-eluting to be separated in just 10 min.

Fig. 7 shows a separation of low levels of chloride (2.5 ppm) and sulfate (2.5 ppm) in the presence of a 200-fold excess of nitrate. The eluent used is again 2.2 m*M* sodium phthalate at pH 6.5. Because the TBP column is very selective for nitrate, the determination of low levels of other early-eluting anions is possible. With most columns, this determination would not be possible because the nitrate would elute too early in the chromatogram. A useful application for this type of determination is in the analysis of nitric acid digests.

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