EFFECT OF CAPACITY ON THE BEHAVIOR OF ANION-EXCHANGE RESINS

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SUMMARY

Strong-base anion exchangers with capacities ranging from 0.04 to 1.46 mequiv./g were prepared from macroporous polystyrene–DVB resins. The capacities were controlled by varying the time of chloromethylation. Distribution ratios of anions decrease with decreasing resin capacity, but selectivity coefficients are essentially constant over the range of capacities studied. The low-capacity resins are shown to be useful for practical chromatographic separations of anion mixtures.

INTRODUCTION

Although porous silica beads coated with an ion-exchange material have been used for separation of ionic organic compounds, most of the work on inorganic ion-exchange chromatography has been carried out with commercially available resins of high capacity. It is remarkable that so little attention has been paid to ion-exchange resins of lower capacity. Only a few reports have appeared which describe or attempt to predict the effect of varying the capacity of a resin[1–3]. These studies were all done with sulfonated cation exchangers. Small *et al.*[4] made practical use of a proprietary anion-exchange resin of low capacity for chromatographic separation of inorganic anions.

This paper describes the preparation and properties of a series of macroporous anion-exchange resins of varying capacity. The results show that anion-exchange resin capacity can easily be varied and that resin capacity is a useful parameter to be considered for practical chromatographic separations.

EXPERIMENTAL

Resin synthesis

The materials used for the synthesis of the anion-exchange resins were macroporous polystyrene–DVB copolymers, XAD-1, 2 and 4, obtained from Rohm and Haas (Philadelphia, Pa., U.S.A.). Batches of the resin beads were ground in a Model 4-E Quaker City mill. The 80–100-mesh particles were removed by dry sieving

and retained for synthesis of the anion-exchange resins. After washing with methanol and water, the resin was slurried with methanol, allowed to settle, and the unsettled fines were decanted.

The air-dried resin was chloromethylated using a procedure described by Goldstein and Schmuckler[5]. A 3-g portion of the resin was swollen with 10 ml of chloromethyl methyl ether. With stirring, 11 ml of methylene chloride, 3 ml of nitromethane and 3 g of zinc chloride were added. The capacities of the anion-exchange resins were controlled by varying the time of chloromethylation, from 5 min to 6 h. All reactions were performed at room temperature except for the highest capacity resin in each XAD series, where the reaction was 6 h at 45–50°. After the appropriate time, the reactions were quenched by adding water. The resins were filtered, washed with water and methanol, and air dried. The resins were then aminated by adding liquified trimethylamine and allowing the amine to evaporate overnight. The final product was washed with 1 M hydrochloric acid, 2-propanol and water, and dried overnight at 60°.

Capacity measurements

Approximately 0.5 g of dry resin was accurately weighed and transferred quantitatively to a small column. The resin was converted to the hydroxide form with approximately 30 bed volumes of 1 M sodium hydroxide and washed with water. Then 1 M sodium chloride was added and the sodium hydroxide in the effluent was titrated with standard hydrochloric acid.

Distribution ratios

Distribution ratios of anions as a function of resin capacity were calculated from retention times measured on a column of the resin. A Dionex System Ten ion chromatograph was used to measure the retention volumes. Pumping was at 30%, which provided an eluent flow of 2.50 ml/min. The sample loop volume was 100 μl. An 80 × 2 mm I.D. column was used for all experiments so that the mobile phase volume and the amount of solid phase would remain constant. A solution of sodium carbonate–bicarbonate in water was used as the eluent. The mobile phase volume was measured by injecting water and noting the volume to the negative water peak.

Selectivity coefficients

Selectivity coeffiients of different anions were measured relative to chloride. The resin was converted to the anion form, air dried, and a weighed amount was shaken for at least 2 h with a measured volume of solution containing known concentrations of the anion and chloride. After equilibration, the chloride remaining in solution was determined by titration with mercuric nitrate. Selectivity coefficients were calculated by assuming that all chloride gone from solution replaced a counter ion on the resin. The ratio of resin counter ion to chloride was high in order to provide a low and fairly consistent conversion of the resin to the chloride form.

RESULTS

Resins prepared

Rohm and Haas XAD-1, -2, and -4 are polystyrene–DVB resins of excellent

physical strength and stable pore structure; they vary in surface area and average pore size (Table I). These resins have found extensive use for sorption of organic impurities from water and for chromatographic use but have not been previously used as a starting material for preparation of anion-exchange resins. The anion-exchange resins used in the present work were made by chloromethylation of XAD resins under mild conditions, followed by alkylation with trimethylamine to produce a quaternary ammonium functional group. The capacities of the resins were varied by controlling the time of the chloromethylation reaction (see Experimental for conditions).

TABLE I

PROPERTIES OF THE RESINS PREPARED

Resin	Surface area (m^2/g)	Av. pore diam. $(\mathring{A})$	Time of chloromethylation (min)	Capacity (mequiv./g)
XAD-1	100	205	—	0.17
			20	0.35
			30	0.41
			90	0.71
			210	0.92
			270	1.01
			300*	1.46
XAD-2	300	90	15	0.22
			60	0.31
			90	0.48
			120	0.59
			300*	0.65
XAD-4	784	50	5	0.13
			10	0.26
			30	0.51
			90	0.63
			300*	0.76

* Reaction temperature was 45–50°. All other reactions were at room temperature.

Table I lists the capacities and chloromethylation times for the anion-exchange resins that were prepared. It was possible to prepare resins of a greater capacity range from XAD-1 as the starting material.

Distribution ratios as a function of resin capacity

Distribution ratios of various anions were measured by a column procedure in which a solution of the anion to be tested was injected onto a column of the XAD anion exchanger that had been conditioned with a sodium carbonate–bicarbonate eluent. The anion was eluted from the column with the same eluent and the retention volume of the anion measured. The mass distribution ratio was then calculated using the equation

$$V_R = V_M(D_m + 1) \tag{1}$$

where V_R is the retention volume, V_M is the holdup volume between the points of injection and detection and D_m is the mass distribution ratio.

Figs. 1 and 2 show distribution ratios for several anions as a function of resin capacity. Because a mixture of two anions had to be used in the eluent, it is not possible to calculate any meaningful selectivity coefficients. However, the results do show that in each case the distribution ratio of the anion increases with increasing capacity. The practical significance is that a much more dilute eluent can be used in column chromatography with a resin of very low exchange capacity.

There is no great difference in resins prepared from XAD-1, -2, or -4. However, the figures show that with XAD-1 resin there is a leveling off of the slope at higher capacity, and in some cases the slope of the plot becomes slightly negative. The selectivity of acetate > iodate is the reverse of the reported selectivity with the gel-type resin Dowex 1-X8. This may be caused by a greater interaction of acetate with the XAD resin matrix, where the ionic functional groups are less concentrated than on the gel resin.

Selectivity coefficients as a function of resin capacity

Selectivity coefficients of nitrate, hydroxide and fluoride relative to the chloride ion were measured for XAD-1 anion-exchange resins of different capacities. A weighed amount of resin in the anion form to be exchanged with chloride was equilibrated with a solution containing known concentrations of that anion and chloride. After equilibration, the chloride in the aqueous phase was determined by titration. The concentration of the other anion in solution and the mole fraction of each anion in the resin phase could then be deduced and the selectivity coefficient calculated.

The exchange reaction (using nitrate as an example) and the selectivity coefficient expression are

$$R\text{-}Cl^- + NO_3^- \rightleftarrows R\text{-}NO_3^- + Cl^- \tag{2}$$

$$K_{Cl}^{NO_3} = \frac{[R\text{-}NO_3^-][Cl^-]}{[R\text{-}Cl^-][NO_3^-]} \tag{3}$$

The selectivity coefficients given in Table II indicate that within a reasonable experimental error the constants do not vary with resin capacity. However, it should be pointed out that the anions studied are all monovalent and strongly hydrated; no selectivity coefficients were measured for hydrophobic anions.

The constancy of selectivity coefficient with resin capacity has useful implications for column chromatography. Suppose that nitrate is injected onto a chloride-form anion-exchange column and that a chloride solution will be used to elute the nitrate. In column chromatography the sample normally uses 1 % or less of the resin capacity; therefore [R-Cl⁻] is essentially constant and equal to the resin capacity. The ratio of $[R\text{-}NO_3^-]$ to $[NO_3^-]$ is a nitrate distribution ratio, D, which can be related to the retention volume for elution of nitrate from the column. The term $[Cl^-]$ will be approximately equal to the eluent chloride concentration, [Eluent]. Substituting these into eqn. 3:

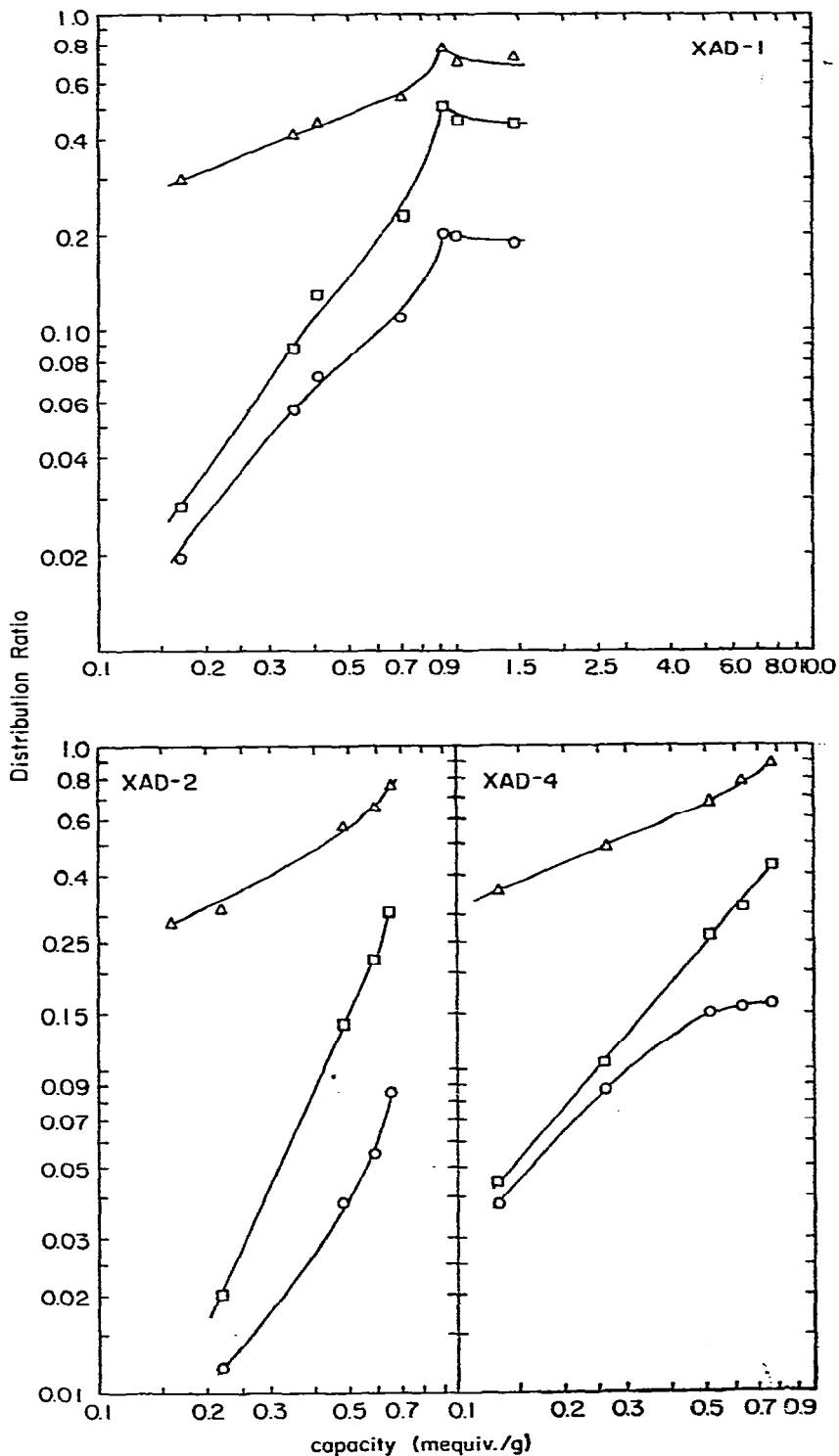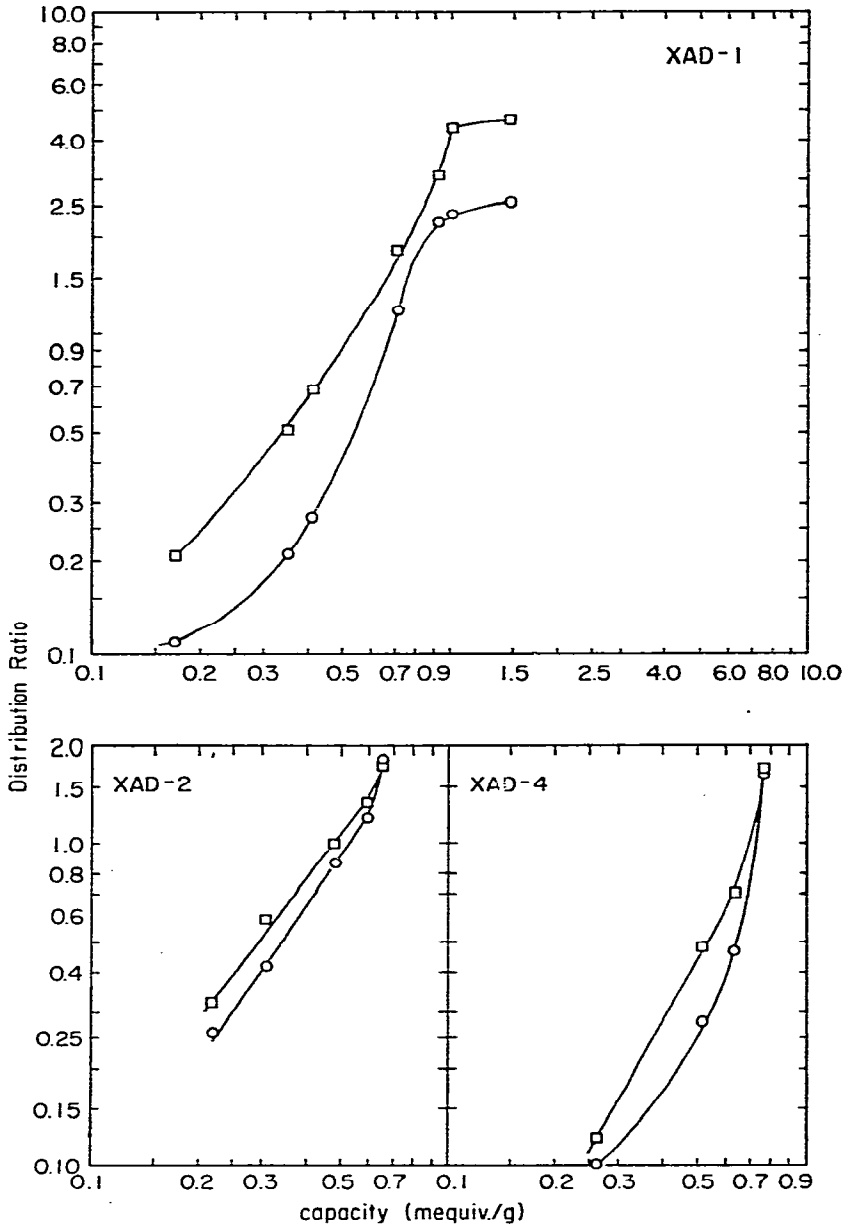$$K_{Cl}^{NO_3} = D \cdot \frac{[Eluent]}{[Cap.]} \tag{4}$$

Fig. 1. Distribution ratios of anions for resins of different capacity. Eluent: $4 \cdot 10^{-4}\,M$ sodium bicarbonate and $3 \cdot 10^{-3}\,M$ sodium carbonate. $\triangle$, Acetate; $\square$, iodate; $\bigcirc$, fluoride.

Fig. 2. Distribution ratios of anions for resins of different capacity. Eluent: $1.2 \cdot 10^{-2}$ M sodium bicarbonate and $1 \cdot 10^{-2}$ M sodium carbonate. □, Sulfate; ○, chloride.

Using this equation, the eluent concentration necessary to obtain any desired value of D can be estimated for a resin of known capacity. It will also be seen that using a resin of lower capacity will reduce the eluent concentration.

Chromatographic separations with low-capacity resins

To demonstrate the applicability of the new resins, a 50 cm × 3 mm I.D. glass

TABLE II

SELECTIVITY COEFFICIENTS FOR XAD-1 ANION-EXCHANGE RESINS OF DIFFERENT CAPACITY

	Capacity XAD-1 (mequiv./g)					
	0.17	0.41	0.71	0.92	1.01	1.46
Mole fraction chloride form	0.04	0.06	0.05	0.05	0.05	0.04
$K_{Cl^-}^{NO_3^-}$	5.0	3.2	3.7	3.7	3.6	4.0
Mole fraction chloride form	0.15	0.13	0.11	0.09	0.09	0.08
$K_{Cl^-}^{OH^-}$	0.10	0.11	0.10	0.11	0.11	0.13
Mole fraction chloride ion	0.22	0.23	0.20	0.16	0.17	0.12
$K_{Cl^-}^{F^-}$	0.08	0.05	0.04	0.05	0.04	0.05

column was packed with 150–160 mesh XAD-1 anion-exchange resin, 0.04 mequiv./g capacity, and the column was connected to a Dionex ion chromatograph. Fig. 3 shows the chromatogram for separation of a sample containing five different anions. The resolution of the sample components is comparable to that obtained using the proprietary commercial resin. The back pressure of the XAD-1 column is quite low (ca. 100 p.s.i.), suggesting the feasibility of using XAD-1 anion resin of a smaller particle size to obtain still better separations.
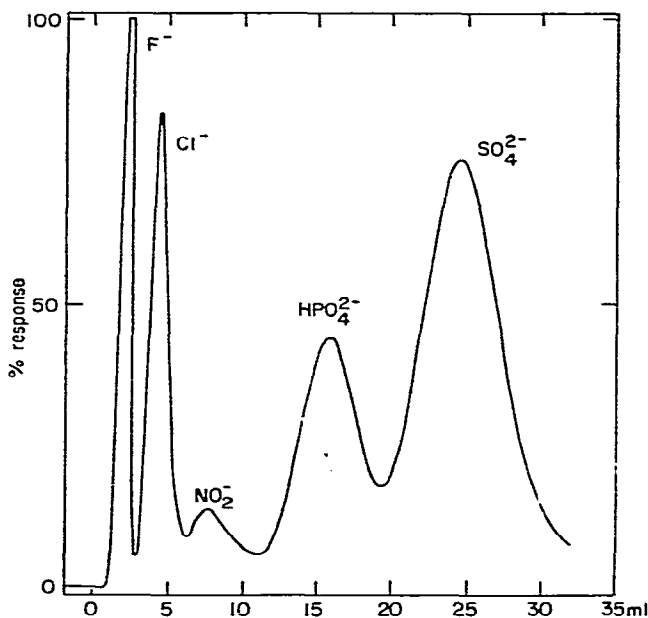

Fig. 3. Separation of fluoride, chloride, nitrite, phosphate and sulfate, respectively on low capacity XAD-1 anion-exchange resin. Resin: 0.04 mequiv./g, 150–160 mesh XAD-1. Column: 50 cm × 3 mm I.D. Eluent: 2.50 ± 0.05 ml/min. 0.0015 M NaHCO$_3$ and 0.0012 M Na$_2$CO$_3$.

DISCUSSION

The three anion-exchange resins act similarly. However, a striking difference between them is that the same reaction conditions produce approximately twice the

capacity when XAD-1 is used as the starting material, rather than XAD-2 or XAD-4. The XAD-1 has lower surface area but larger pores than the others.

The leveling off of XAD-1 distribution ratios at higher capacities may be due to the more efficient retention of carbonate by the resin. At the higher capacities the resin functional groups are closer together and the carbonate can more easily combine with two resin functional groups.

Perhaps the most significant accomplishment of this work has been to demonstrate the effect of capacity on the eluent concentration needed to elute anions in column chromatography. A resin of lower capacity permits the use of a lower eluent concentration. The capacity of XAD anion-exchange resins can be easily varied, making this a parameter that can be changed to permit elution of anions that normally are held tightly by a resin.

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