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## SELECTIVITY BEHAVIOR OF LOW-CAPACITY, PARTIALLY SULFO- NATED, MACROPOROUS RESIN BEADS

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### SUMMARY

Cation-exchange resins with capacities ranging from 0.23 to 3.70 mequiv./g were prepared by sulfonation of highly cross-linked macroporous polystyrene resins. Distribution coefficients for exchange of hydrogen-form resin for polyvalent metal cations in 1 *M* acid show marked increases with increasing resin capacity.

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### INTRODUCTION

Most of the work that has been done on analytical ion-exchange separations has been carried out with commercially available resins of high capacity. Although superficially porous silica beads coated with an ion-exchange material have recently been used for organic chromatographic separations, it is remarkable that so little attention has been paid to conventional ion-exchange resins of lower capacity. A few authors have prepared and characterized partially sulfonated ion-exchange resin beads<sup>1-4</sup>. The results have indicated that unless the beads are of very low cross-linking and much care is taken, sulfonation occurs to different extents within single beads and among different beads in the same reaction mixture. A few measurements of distribution data or selectivity coefficients for exchanges on these resins have been reported. Skafi and Lieser<sup>5-7</sup> also prepared sulfonated cation-exchange resins of low capacity and obtained some excellent practical separations. They found the kinetics of these resins to be very favorable.

This work describes the preparation of low-capacity, partially sulfonated macroporous cation-exchange resins and the measurement of distribution data and selectivity coefficients of multivalent metal ions on these resins. Macroporous resins are chemically and mechanically stable. They swell and shrink very little and the liquid content is essentially the same no matter what the liquid<sup>8</sup>. These properties make such resins ideal for modern forced-flow chromatography.

### EXPERIMENTAL

#### *Beads*

The copolymer material used in this study for the preparation of partially sulfonated ion-exchange beads was the commonly used poly(styrene-divinylbenzene) copolymer.

The beads were obtained in 150–300  $\mu$  size from Rohm and Haas (Philadelphia, Pa., U.S.A.) as XAD-2. This and other macroreticular copolymer beads marketed by the same company have been well characterized. XAD-2 resin beads have a surface area of 300 m<sup>2</sup>/g of copolymer and an average pore diameter of 90 Å.

### Reagents

Reagents used were those normally found in the laboratory. The stock metal ion solutions used in these determinations were prepared by dissolving reagent-grade nitrates, or perchlorates in water to produce stock solutions which were approximately 0.1 *M* and were then standardized by titration with EDTA. The solutions used in the batch equilibrations were then prepared by diluting aliquots of the stock solutions and of the desired background acid to volume in a volumetric flask to produce a solution approximately  $1 \times 10^{-3}$  *M* in the desired metal.

### Procedure

Since the data of Reichenberg<sup>3</sup> and others indicated that homogeneous beads are very difficult to prepare, no attempt was made to prepare completely homogeneous beads.

Batches of the beads were taken as received in the 150–300  $\mu$  size and placed in a Model 4-E Quaker City Mill and ground until they were all approximately 200–400 mesh. They were then dry-sieved and the portion not passing through the 250-mesh sieve was placed back in the mill for further grinding. The 250–325 mesh (44–63  $\mu$ ) size beads were removed for sulfonation.

The 250–325 mesh beads were washed with water, ethanol, and acetone, and vacuum-dried. Portions of 2–10 g of the copolymer were taken and placed in 50–100 ml of concentrated sulfuric acid. The beads were then sulfonated at various temperatures ranging from 2 to 175 ° for varying lengths of time.

The reaction mixture was then placed in a suction filter and the liquid rapidly removed. The beads were washed several times with water, methanol, and acetone, and air-dried. Extreme fines were removed by flotation in methanol.

Measurements of the dry weight of a quantity of resin in the hydrogen form were made by two different methods, *viz.* (1) vacuum-drying in a desiccator at 60 ° overnight and (2) air-drying in a suction filter after washing with ethanol and acetone.

In no case did the weights obtained by the two methods differ by more than 0.5%. The second method, being the simpler, was then used for all subsequent weight determinations.

The weight capacity of the dry hydrogen-form resin was determined by placing a weighed quantity of the dry hydrogen-form resin in a solution containing a stoichiometric excess of sodium hydroxide and back-titrating the excess with standard hydrochloric acid. Capacities of the twelve resins, determined by this method, ranged from 0.23 to 3.70 mequiv./g.

The capacity and monofunctionality of the resins were then checked by direct pH titration. The titrations of each of the resins were performed in 1 *M* KNO<sub>3</sub> using 0.1113 *M* NaOH as the titrant. Values of capacity determined by direct titration of the resins agreed within 1% of those obtained by the first method.

### *Measurement of equilibria*

All determinations of the distribution ratio or selectivity coefficient were made at a loading of less than 1% of the total capacity of the resin. Distribution ratios of metal ions on the various resins were determined by both the batch and the column method. In the batch method about 3 g of dry hydrogen-form resin was weighed and added to 20 ml of a dilute solution of the metal ion. The mixtures were then shaken for at least 1.5 h. The mixtures were then centrifuged and part of the supernatant liquid was removed by pipet for analysis. The amount of metal ion remaining in the supernatant was then determined by the appropriate EDTA titration method.

The second method of obtaining distribution ratios for metal ions on the resins involved measurement of the recorded column elution volumes by means of forced-flow chromatography. The elution volume is related to the weight distribution coefficient by the expression

$$\bar{v} = D(W) + V_m$$

where  $\bar{v}$  is the elution volume to the peak maximum,  $D$  is the weight distribution coefficient,  $W$  is the weight of resin in the column, and  $V_m$  is the total volume of mobile phase between injection and detection points. Thus the distribution coefficient is expressed as:

$$D = \frac{\bar{v} - V_m}{W}$$

A Chromatronix LC-6M-13 column (Chromatronix, Berkeley, Calif., U.S.A.) was used for these determinations. The column was dry-packed or slurry-packed with 2-3 g of resin and conditioned with a suitable aqueous solution. The mobile phase volume was measured by injecting a 56- $\mu$ l sample of water into the column containing 1  $M$  hydrochloric acid and noting the volume required for a pH change to occur in the detector. (This was done by noting the color change of an Arsenazo III solution in 2  $M$  ammonia that was added to the column effluent through a mixing-chamber just ahead of the detector.) Distribution coefficients for metal ions were determined by injecting a 56- $\mu$ l sample of the metal ion solution and noting the volume required for elution to the peak maximum.

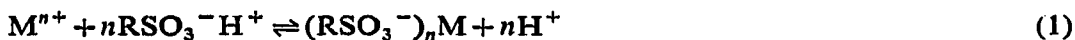
## RESULTS AND DISCUSSION

It would be interesting and useful to be able to explain how resin capacity affects the ion-exchange process including selectivity. In discussing theories of ion-exchange selectivity Reichenberg<sup>3</sup> emphasizes the Eisenman theory, which holds that selectivity arises both from electrostatic interaction between the fixed groupings and the counter ion (the exchangeable ion), and also from the differences in free energies needed to remove or rearrange water molecules around the fixed groupings and the counter ions. The latter consideration (hydration free energy change of counter ions) appears to determine the selectivity of sulfonic acid cation exchangers. Reichenberg feels that a significant fraction of counter ions undergo some degree of solvent stripping and that this is brought about by attractive interactions of

fixed groupings with the counter ions. Only ions that touch (or nearly touch) fixed groupings make a significant contribution to selectivity in Reichenberg's view.

Diamond and Whitney<sup>9</sup> treat the resin phase as a concentrated electrolyte solution but emphasize the role of water in solvating the smaller ion and forcing the larger one into the more poorly solvating resin phase. In their opinion, touching of fixed groupings and counter ions is not a significant factor in determining selectivity.

According to these theories, increased capacity (more fixed sulfonate groups) would increase differences in hydration of  $H^+$  and  $M^{n+}$  and would increase the selectivity of the resin for the metal ion. Distribution coefficients were determined for the exchange



at fixed hydrogen ion concentration (1 *M*) and with resins of varying capacity. The plots in Figs. 1 and 2 show that the distribution coefficients increase with increased resin capacity, first slowly and then much more rapidly at the higher capacities.

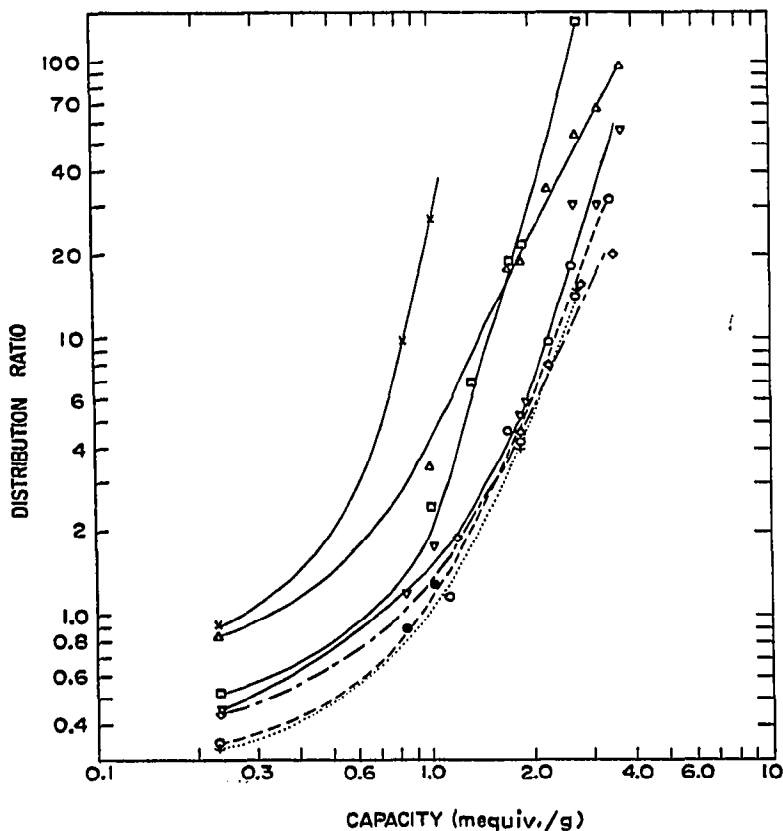


Fig. 1. Distribution coefficients of metal ions in 1 *M*  $HClO_4$  of different capacity.  $\Delta$ , Aluminum(III);  $\times$ , lead(II);  $\square$ , calcium(II);  $\nabla$ , copper(II);  $\circ$ , zinc(II);  $\diamond$ , magnesium(II);  $+$ , nickel(II).

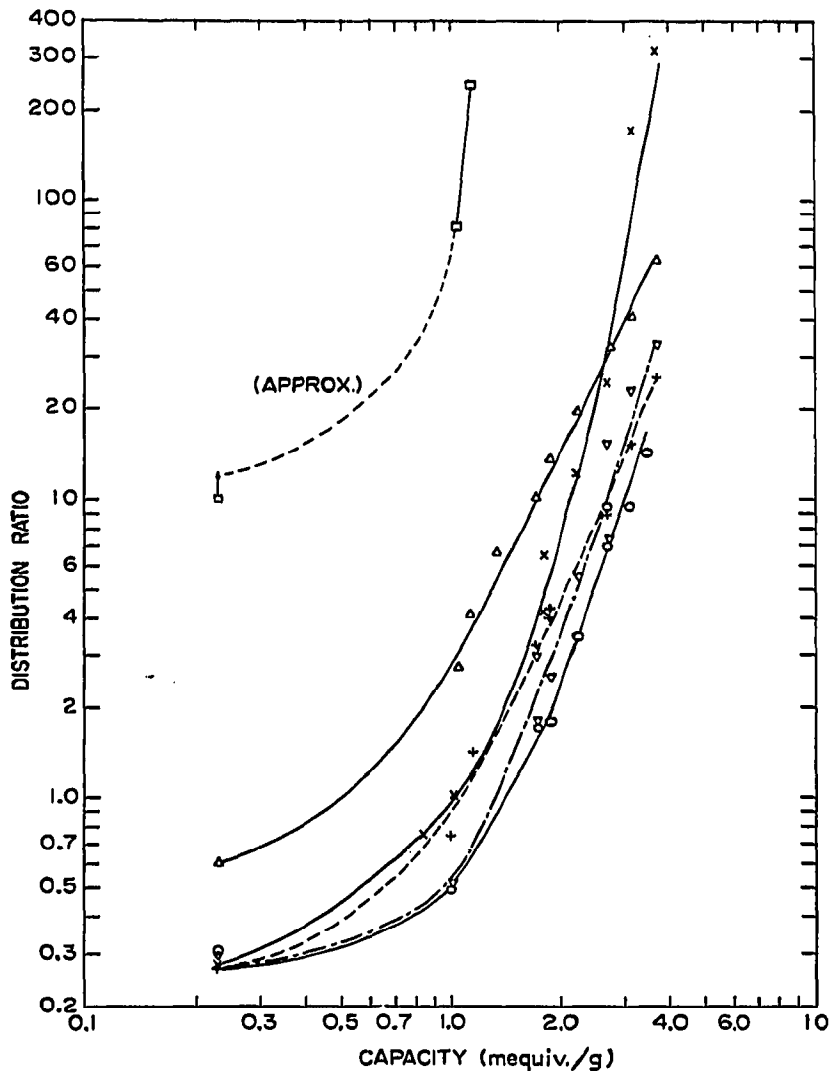


Fig. 2. Distribution coefficients of metal ions in 1 *M* HCl for resins of different capacity. □ Thorium(IV); Δ, aluminum(III); ×, lead(II); +, nickel(II); ▽, copper(II); ○, zinc(II).

Previous workers have calculated selectivity coefficients (instead of distribution coefficients) as a function of resin capacity. It has been shown that increasing capacity of cation-exchange resins increases the selectivity coefficient,  $K_{M/H}$ , for exchange of a metal ion for a hydrogen ion<sup>1</sup>. However, the magnitude of the selectivity coefficient change is small and the data that have been reported are quite limited.

For exchange reaction 1 the selectivity coefficient expression is

$$K_{M/H} = \frac{[(\text{RSO}_3^-)_n\text{M}]}{[\text{M}^{n+}]} \cdot \frac{[\text{H}^+]^n}{[\text{RSO}_3^- \text{H}^+]^n} \quad (2)$$

Substituting the distribution coefficient,  $D$ , for the left-hand terms and representing  $[\text{RSO}_3-\text{H}^+]$  as  $[\text{Cap}]$ , the resin capacity, eqn. 2 becomes

$$K_{M/H} = \frac{D[\text{H}^+]^n}{[\text{Cap}]^n} \quad (3)$$

Our results, calculated using eqn. 3, are shown in Fig. 3. The results indicate a decrease in the selectivity coefficients with increased capacity, followed by an increase in selectivity coefficients to higher values. Behavior of this type has not previously been reported for selectivity coefficients with varying resin capacities. It should be noted, however, that calculation of the selectivity coefficients is strongly dependent on the power to which the resin capacity must be raised in eqn. 3. In our calculations the power,  $n$ , was the charge on the free metal ion.

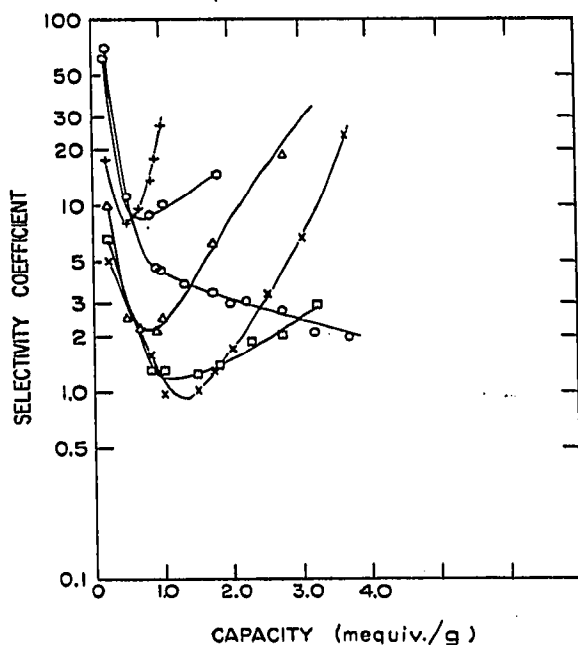


Fig. 3. Selectivity coefficients as a function of resin capacity.  $\times$ , Pb, 1  $M$  HCl;  $+$ , Pb, 1  $M$  HClO<sub>4</sub>;  $\circ$ , Al, 1  $M$  HClO<sub>4</sub>;  $\Delta$ , Ca, 1  $M$  HClO<sub>4</sub>;  $\square$ , Zn, 1  $M$  HClO<sub>4</sub>;  $\diamond$ , Lu, 1  $M$  HNO<sub>3</sub>.

Since the changes in selectivity coefficients with resin capacity previously reported<sup>1</sup> have been small, it was next assumed that our selectivity coefficients are approximately constant. Then rearrangement of eqn. 3 gives

$$D = \frac{[\text{Cap}]^n K_{M/H}}{[\text{H}^+]^n} \quad (4)$$

$$\log D = n \log [\text{Cap}] - n \log [\text{H}^+] + \log K_{M/H} \quad (5)$$

A plot of  $\log D$  vs. the resin capacity at fixed  $H^+$  concentration should give a linear plot with slope equal to  $n$ . The plots in Figs. 1 and 2 show considerable curvature at lower capacities, but they do have an approximately linear portion at the medium to higher capacities. The slopes of these linear sections are greater than the metal ion charge in every case except for  $Al^{3+}$ . The slopes also increase with increasing crystalline ionic radii of the metal ions (Table I).

TABLE I  
COMPARISON OF MAXIMUM SLOPES OF PLOTS IN FIG. 1 WITH CRYSTALLINE IONIC RADII

<i>Metal ion</i>	<i>Slope</i>	<i>Ionic radius (A)</i>
$Pb^{2+}$	5.0	1.20
$Ca^{2+}$	4.5	0.99
$Zn^{2+}$	3.95	0.74
$Cu^{2+}$	3.5	0.73
$Ni^{2+}$	3.6	0.72
$Mg^{2+}$	2.3	0.65
$Al^{3+}$	2.5	0.50

These facts suggest the possibility at least that more resin sulfonate groups than required for charge neutralization are somehow associated with the metal ion. If such an association is a reality, hydrogen ions from the resin are probably in the associated species to give it electro-neutrality. This conclusion does not seem to fit very well with the leading theories of ion-exchange selectivity and may, of course, be in error. However, it is a fact that the distribution coefficients increase with a rather high power of resin capacity and this should prove to be of practical value.

In conclusion, ion-exchange resin capacity can easily be varied, and this introduces a new parameter to be considered when devising practical analytical separations. Some separation factors may be more favorable using resins of lower capacity. Metal ions such as thorium(IV) can be more easily eluted or can be eluted at lower acid or salt concentrations using lower capacity resins. Since the sulfonic acid groups on lower capacity resins may be more readily accessible, exchange kinetics may be more rapid on these resins. Some of these points will be demonstrated in forthcoming papers.

#### ACKNOWLEDGEMENTS

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