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METAL ION SELECTIVITY ON SULFONATED CATION-EXCHANGE RESINS OF LOW CAPACITY

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SUMMARY

Although ion chromatography has become a popular analytical method, quantitative data for retention of metal cations by modern ion-exchange resins are rather limited. In the present work, the selectivity of low-capacity, sulfonated resins is determined. Electron micrographs have shown the functional groups to be concentrated near the outer perimeter of these resin beads.

A column packed with a 12% cross-linked polystyrene cation exchanger, 6.1 $\mu\text{equiv./g}$ capacity, was used to obtain retention data for 36 metal cations. Adjusted retention times are given for these cations for 8 different concentrations of perchloric acid eluents, ranging from 0.10 to 1.00 *M*. Linear plots were obtained for log adjusted retention time vs. log eluent ion activity. In almost every case the slope was close to the theoretical slope of -2 for divalent metal ions and -3 for trivalent metal ions. The adjusted retention times of metal cations were also obtained with eluents containing Na^+ , Mg^{2+} , $[(-\text{CH}_2\text{NH}_3)_2]^{2+}$, and $[\text{C}_6\text{H}_5\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3]^{2+}$ perchlorates. These data permit comparison of various selectivity coefficients as a function of the eluent cation. Finally, the adjusted times are reported for 32 metal cations using resins of 3 different capacities, with a 0.75 *M* perchloric acid eluent.

INTRODUCTION

The selectivity of sulfonated ion-exchange resins for metal cations is often qualitatively expressed in terms of elution orders. Numerical selectivity data for cations are limited^{1,2}. Strelow and co-workers³⁻⁵ published comprehensive lists of distribution coefficients for metal ions with perchloric acid and other mineral acid eluents. However, their data are for sulfonated gel resins of high exchange capacity.

The main purpose of the present work is to provide comprehensive quantitative

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data on the affinity of metal cations for the type of sulfonated ion-exchange resins now used for ion chromatography. These resins are small, spherical beads and have a much lower exchange capacity than the classical resins. Such information will be useful for practitioners of modern ion chromatography and for those interested in the theoretical aspects of selectivity of these resins for various cations.

EXPERIMENTAL

Eluent preparation

All eluents were prepared with Type I reagent-grade water from a cartridge water purification system (Barnstead, Boston, MA, U.S.A.).

Concentrated reagent-grade perchloric acid (70%) was used to prepare all perchloric acid eluents and to adjust the pH of all other eluents. Perchloric acid eluents were prepared from a stock solution, filtered through a 0.45- μm membrane filter (as in the case of all eluents) and degassed under suction. The hydrogen ion concentration in each eluent was determined by titration with tris(hydroxymethyl)-aminomethane. Acids more concentrated than 1.0 *M* corroded the equipment and gave too little retention.

Sodium and magnesium perchlorate eluents were prepared from reagent-grade bicarbonate and carbonate salts, respectively. The appropriate amount of salt was dissolved, diluted to near the final volume, and the pH adjusted to 2.5. The solution was then diluted, mixed thoroughly and the pH adjusted to 2.5 with 50% aq. perchloric acid solution, if necessary. Each eluent was then filtered and degassed under suction.

Ethylenediamine eluents were prepared from reagent-grade amine after redistillation. *m*-Phenylenediamine was converted to the dihydrochloride and recrystallized. Dilution and pH adjustment was done in the same manner as with the sodium and magnesium perchlorate eluents.

Post-column reagents

Most of the metals examined were detected using 0.125% pyridylazoresorcinol (PAR) in 2.0 *M* ammonium hydroxide–1.0 *M* ammonium acetate buffer. Arsenazo III (0.0375%) in 0.5 *M* sodium acetate was used as an alternate to PAR. The Arsenazo III reagent gave good results for strontium and barium. Arsenazo I (0.0175%) in ammonium hydroxide (3.0 *M*) showed good sensitivity for detection of magnesium and calcium. All color-forming reagents were diluted with Type I reagent grade water and filtered through a 0.45- μm filter before use.

Cation-exchange resins

Cation-exchange resins were 12% crosslinked poly(styrene–divinylbenzene) gel beads; 12–15 μm in diameter. The resins were obtained from James Benson (Reno, NV, U.S.A.). Eluent studies were run using a resin with a bulk ion-exchange capacity of 6.1 $\mu\text{equiv. per g.}$ Sulfonation of the resin beads has been described previously⁶. The resins are, in fact, only functionalized to a depth of about 50 Å into the bead as shown by scanning transmission electron microscopy⁶. These beads are essentially pellicular in nature.

Metal ion solutions

All metal stock solutions were prepared from highest purity reagent grade salts available and an appropriate amount of perchloric acid was added to the solutions to prevent hydrolysis.

Rare earth solutions were prepared from the oxides of purity of at least 99.99% (Dr. J. E. Powell, Ames Laboratory, Ames, IA, U.S.A.). Dissolution of each oxide was with the appropriate acid.

Retention times were measured from 20- μ l injections of 0.20 mM metal ion solutions. In all dilutions enough perchloric acid was added to prevent hydrolysis.

Apparatus

The instrument was modular in design. The eluent delivery system included a single-piston pump (Milton Roy, Riviera Beach, FL, U.S.A.) and a injection valve (Rheodyne, Cotati, CA, U.S.A.) with a 20- μ l fixed sample loop. A pressure relief valve (Swagelok, Cleveland, OH, U.S.A.) and a coil pulse dampener (LiChroma Damp, Norristown, PA, U.S.A.) were placed in a parallel configuration between the pump and the injection valve.

Chromatographic columns (25 cm \times 2 mm I.D.) were of thick-walled glass (Rainin Instrument, Woburn, MA, U.S.A.). The columns were packed with the low-capacity, surface sulfonated cation exchange resin. An upward slurry packing method of packing columns was used as described by Barron⁷. The slurry liquid was ethylene glycol-water (45:55, v/v). After packing, the column was flushed with distilled-deionized water. Minimal bed compression was observed. Columns were maintained at 25°C during use and allowed to equilibrate with the eluent for at least 1 h before use.

Metal cations were detected by post-column reaction with color-forming reagents. The reaction chamber was the same as that used by Elchuk and Cassidy⁸. Intimate mixing of the column effluent and the reagent was obtained in a minimum dead volume (est. 2 μ l).

Color-forming reagents were delivered to the mixing tee with either a chemically inert, "valveless" pump (FMI, Oyster Bay, NJ, U.S.A.) or a peristaltic pump (Rainin Instrument). All reagent delivery lines in the post-column reaction system were of PTFE, polypropylene, or poly(vinyl chloride). Pump pulsations were dampened using a home-made debubbling column and a diaphragm-type pulse dampener. The spectrophotometric detector was a Kratos (Ramsey, NJ, U.S.A.) Model 783 scanning UV-VIS detector equipped with a 12- μ l flow cell. The chromatographic system has a flow-rate of 1.0 ml/min, as did the post-column reagent delivery system. The dead volume of the system was 0.495 ml.

RESULTS

Elution with perchloric acid and sodium perchlorate

The approach taken is to measure retention times of metal cations on columns containing low-capacity resins with eluents containing perchloric acid or various perchlorate salts. The perchlorate anion is used to eliminate any possible complexing of a metal ion by the eluent anion. Capacity factors (k') are calculated from the retention data.

Eluents containing hydrogen ions or sodium ions were used at concentrations

ranging from 0.10 to 1.0 *M*. In general, narrow chromatographic peaks were obtained, although the rare earth peaks were broad with some tailing.

The capacity factors were calculated from the retention times and are given in Tables I and II. The data show that, as expected, eluents containing sodium(I) are more efficient than those containing hydrogen(I). The data in these tables are arranged in order of increasing capacity factors. In this way it is possible to compare the relative affinities of the various divalent and trivalent metal ions for resin sites.

TABLE I
CAPACITY FACTORS (k') FOR VARIOUS CATIONS USING PERCHLORIC ACID ELUENTS

Cation	Perchloric acid concentration (<i>M</i>)							
	1.00	0.85	0.75	0.60	0.50	0.40	0.25	0.10
V(IV)	0.08	0.10	0.12	0.16	0.28	0.40	0.91	5.23
Be(II)	0.10	0.18	0.24	0.30	0.38	—	1.86	4.59
Zr(IV)	0.14	0.20	0.24	0.38	0.65	0.95	2.00	13.31
Mg(II)	0.16	0.18	0.26	0.36	0.51	0.67	1.39	7.49
Fe(II)	0.16	0.18	0.26	0.38	0.53	0.85	1.94	9.19
Mn(II)	0.16	0.18	0.26	0.42	0.55	0.95	2.02	12.14
Hg(II)	0.16	0.18	0.30	0.42	0.69	0.99	2.99	11.70
Ni(II)	0.16	0.22	0.28	0.38	0.59	0.89	2.00	12.75
Zn(II)	0.12	0.18	0.30	0.46	0.71	0.97	2.55	12.67
Cu(II)	0.16	0.22	0.32	0.52	0.61	0.97	3.19	12.83
U(VI)	0.16	0.22	0.28	0.40	0.67	0.99	3.52	12.83
Co(II)	0.20	0.22	0.28	0.38	0.48	1.05	2.02	13.56
Cd(II)	0.22	0.28	0.32	0.59	0.77	1.39	3.56	25.25
Ca(II)	0.32	0.40	0.57	0.97	1.47	2.26	5.98	21.41
Sr(II)	0.44	0.66	0.81	1.39	2.06	3.09	8.55	35.35
Ba(II)	1.01	1.29	1.52	2.73	3.94	6.63	15.76	—
Pb(II)	1.21	1.64	1.90	2.99	4.75	7.37	28.48	100.0
Al(III)	0.68	1.01	1.60	2.95	5.27	9.90	43.0	—
Fe(III)	1.07	1.68	2.89	5.54	9.98	18.42	80.0	—
V(III)	1.13	2.00	2.89	4.67	10.10	20.08	—	—
In(III)	1.15	2.12	3.05	5.84	10.59	19.84	63.8	—
Lu(III)	2.67	4.71	6.57	13.07	27.1	50.5	—	—
Yb(III)	2.93	5.15	7.17	14.14	28.7	52.5	—	—
Tm(III)	2.97	5.25	7.54	14.75	28.9	57.0	—	—
Y(III)	3.13	5.94	8.18	16.38	30.1	59.6	—	—
Er(III)	3.13	5.31	7.92	15.72	30.5	59.8	—	—
Ho(III)	3.37	5.62	8.59	16.71	32.9	63.4	—	—
Dy(III)	3.78	6.10	9.25	18.61	35.8	70.9	—	—
Gd(III)	4.89	8.40	12.48	24.65	47.7	91.3	—	—
Eu(III)	5.45	9.25	13.84	27.47	52.9	105.0	—	—
Sm(III)	6.04	11.37	15.43	30.30	59.4	116.0	—	—
Nd(III)	7.13	13.64	17.76	35.35	69.3	137.8	—	—
Pr(III)	7.44	14.22	18.57	37.58	71.3	142.2	—	—
Ce(III)	8.69	14.44	21.2	43.2	80.8	167.7	—	—
La(III)	9.68	15.64	23.8	47.9	93.7	187.7	—	—
Bi(III)	8.75	13.1	21.2	31.9	53.7	135	—	—

TABLE II
CAPACITY FACTORS (k') OF VARIOUS CATIONS USING SODIUM PERCHLORATE ELUENTS

Cation	Sodium perchlorate concentration (M)				
	1.00	0.75	0.50	0.25	0.20
Be(II)	0.06	0.06	0.12	—	1.05
Mg(II)	0.06	0.10	0.18	0.73	1.23
Ni(II)	0.06	0.14	0.26	1.09	2.42
Fe(II)	0.08	0.14	0.32	1.15	3.58
Co(II)	0.08	0.16	0.20	1.25	2.79
Zn(II)	0.10	0.12	0.30	1.03	2.20
Hg(II)	0.10	0.18	0.36	1.11	2.95
Zr(IV)	0.12	—	0.30	1.29	2.71
V(IV)	0.14	0.16	1.37	0.95	2.40
Mn(II)	0.16	0.20	6.26	1.21	3.45
Cd(II)	0.16	0.22	0.67	1.49	3.23
Ca(II)	0.18	0.30	0.48	2.06	4.36
Cu(II)	0.20	0.30	0.46	1.31	2.79
Sr(II)	0.28	0.51	0.97	3.62	5.92
U(VI)	0.61	0.87	1.27	3.54	7.25
Ba(II)	0.75	1.21	2.26	4.46	—
Al(III)	—	0.75	2.32	—	—
Pb(II)	1.15	1.51	3.03	—	27.7
Lu(III)	1.31	2.63	6.91	44.24	—
Yb(III)	1.37	2.87	7.29	62.6	—
Tm(III)	1.56	3.03	7.92	64.8	—
Y(III)	1.54	2.95	8.28	65.0	—
Er(III)	1.62	3.03	8.34	67.1	—
Ho(III)	1.66	3.31	8.95	67.9	—
Dy(III)	1.94	3.98	10.85	86.1	—
Tb(III)	2.19	4.12	11.33	88.9	—
Gd(III)	2.51	4.89	13.19	104.0	—
Eu(III)	2.79	5.49	14.71	116.2	—
Sm(III)	3.29	6.00	16.55	123.6	—
Nd(III)	3.13	6.24	16.85	131.7	—
Pr(III)	3.21	6.20	17.92	138.6	—
Ce(III)	3.33	6.83	20.40	147.7	—
La(III)	3.80	7.86	21.42	173.5	—
In(III)	3.33	5.01	—	—	—

Note that there are crossovers in the capacity factors of lead(II) and several trivalent metal ions as the eluent concentration is increased.

The elution order of metal ions reported in Table I is similar to that reported earlier by Strelow and Sondorp⁵ with perchloric acid eluents and gel resins of high exchange capacity. Strelow and co-workers noted anion-complexing effects on elution orders in several cases when eluent acids other than perchloric acid were used.

Ion-exchange equilibrium

The following expression can be written for a cation-exchange equilibrium:



where y is the charge of the metal ion, M , x is the charge of the eluent cation, E , and barred terms represent ions in the resin phase. The equilibrium constant for this exchange may be written,

$$K_E^M = \frac{[E]^y [\bar{M}]^x}{[\bar{E}]^y [M]^x} \quad (2)$$

where brackets represent the activities of the ions.

If the cation under study is in very low concentration and the eluent contains a fully dissociated electrolyte, then the portion of the ion-exchange isotherm is linear⁹. For a monofunctionalized ion exchanger, linearity should be maintained as long as a near-equilibrium state is maintained¹⁰.

In eqn. 2 the ratio of $[\bar{M}]$ to $[M]$ is proportional to the capacity factor, k' , and $[\bar{E}]$ times x is the resin capacity, C . Inserting these into eqn. 2, rearranging and converting to logarithms gives the expression,

$$\log k' = \frac{-y}{x} \log \{E\} + \frac{y}{x} \log C + \log \text{constant} \quad (3)$$

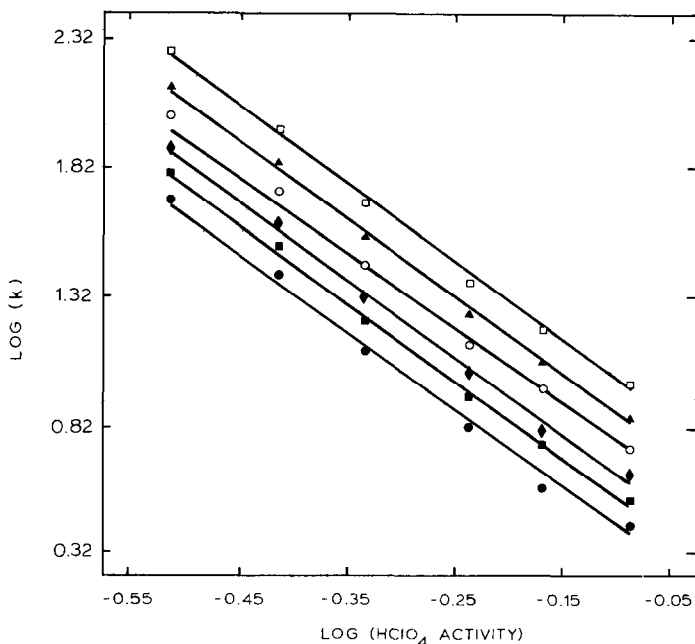


Fig. 1. Plots of $\log k'$ vs. \log of perchloric acid activity for several rare earth 3+ ions. ● = Lu; ■ = Ho; ◆ = Tb; ○ = Eu; ▲ = Nd; □ = La.

Eqn. 3 predicts that a plot of $\log k'$ against the activity of the eluent ion should be a straight line with a slope of $-y/x$. If the eluent ion is monovalent, the slope should be $-y$, where y is the charge on the metal ion, M.

The data in Table I (perchloric acid eluent) and Table II (sodium perchlorate eluent) were plotted according to eqn. 3. Linear plots were obtained in all cases. (See Fig. 1 for an example). The slopes, obtained by linear regression, are given in Table III for perchloric acid and in Table IV for sodium perchlorate. In most cases the

TABLE III

LINEAR REGRESSION DATA FOR $\log k'$ PLOTTED AGAINST $\log [\text{HClO}_4]$

Cation	Slope		<i>r</i>
	<i>This work</i>	<i>Ref.*</i>	
Be(II)	-1.64	-1.02	-0.990
Mg(II)	-1.66	-1.25	-0.998
Ca(II)	-1.87	-1.54	-0.996
Sr(II)	-1.91	-1.66	-0.998
Ba(II)	-1.97	-1.92	-0.997
Mn(II)	-1.89	-1.36	-0.998
Zn(II)	-1.98	-1.32	-0.998
Ni(II)	-1.87	-1.35	-0.998
U(VI)	-1.96	-1.32	-0.996
Cu(II)	-1.92	-1.33	-0.997
Fe(II)	-1.79	-1.36	-0.999
Co(II)	-1.86	-1.34	-0.992
Cd(II)	-2.08	-1.40	-0.997
V(IV)	-1.83	-1.11	-0.997
Pb(II)	-2.00	-1.88	-0.994
Hg(II)	-1.92	-1.76	-0.997
Zr(IV)	-1.95	-	-0.999
Al(III)	-2.88	-1.80	-0.999
Bi(III)	-2.67	-2.24	-0.992
Fe(III)	-2.99	-1.81	-1.000
In(III)	-2.78	-1.87	-0.999
V(III)	-2.87	-	-0.996
Lu(III)	-3.00	-	-0.998
Yb(III)	-2.95	-	-0.998
Tm(III)	-2.99	-	-0.999
Y(III)	-2.95	-2.20	-0.999
Er(III)	-3.00	-	-0.999
Ho(III)	-3.01	-	-0.999
Dy(III)	-3.01	-2.23	-0.999
Tb(III)	-3.04	-	-0.998
Gd(III)	-2.97	-	-0.999
Eu(III)	-3.01	-	-0.999
Sm(III)	-2.97	-	-0.999
Nd(III)	-2.97	-	-0.998
Pr(III)	-2.95	-	-0.998
Ce(III)	-3.01	-2.48	-0.999
La(III)	-3.04	-2.49	-0.999

* Calculated from data of Strelow and Sondorp⁵.

TABLE IV

LINEAR REGRESSION DATA FOR $\log k'$ PLOTTED AGAINST $\log [\text{NaClO}_4]$

<i>Cation</i>	<i>Slope</i>	<i>Correlation coefficient</i>
Be(II)	-2.06	-0.975
Mg(II)	-2.04	-0.998
Ca(II)	-2.11	-0.991
Sr(II)	-2.05	-0.999
Ba(II)	-1.75	-1.000
Ni(II)	-2.38	-0.995
Fe(II)	-2.44	-0.989
Co(II)	-2.34	-0.983
Zn(II)	-2.12	-0.991
V(IV)	-1.95	-0.952
Hg(II)	-2.15	-0.990
Zr(IV)	-2.10	-0.998
Mn(II)	-2.03	-0.960
Cd(II)	-1.99	-0.989
Cu(II)	-1.70	-0.987
U(VI)	-1.62	-0.986
Pb(II)	-2.24	-0.990
In(III)	-3.09	-0.998
Lu(III)	-2.80	-0.999
Yb(III)	-3.03	-0.997
Tm(III)	-2.98	-0.997
Y(III)	-3.00	-0.998
Er(III)	-2.99	-0.997
Ho(III)	-2.96	-0.999
Dy(III)	-3.02	-0.998
Tb(III)	-2.98	-0.998
Gd(III)	-2.98	-0.998
Eu(III)	-2.98	-0.998
Sm(III)	-2.94	-0.998
Nd(III)	-2.97	-0.998
Pr(III)	-3.00	-0.998
Ce(III)	-3.02	-0.999
La(III)	-3.04	-0.998

negative slope was very close to the charge on the metal ion. The somewhat low values obtained for Be(II) and Bi(III) in Table III may be due to partial hydrolysis of the metal cation. The slopes obtained for vanadium(IV) and zirconium(IV) indicate that the metal ions are present as VO^{2+} and ZrO^{2+} , respectively.

The necessity for using the activity of the eluent should be emphasized. When the concentration of H^+ (in HClO_4) was used, the slopes for the rare earths were approximately -3.25 . However, the slopes obtained using the activity were very close to the theoretical value of -3.0 .

In view of the very low capacity of the resin used, it may seem remarkable that slopes so close to the theoretical values were obtained. One might expect the ion-

exchange sites to be so scattered that it would be impossible for a 3+ cation to exchange with three sites. However, other work⁶ has demonstrated that the exchange sites are in a thin layer on the outer perimeter of the ion-exchange bead. The results obtained here indicate that the concentration of sites in this outer layer is sufficiently dense that essentially theoretical exchange is obtained for polyvalent metal ions.

It is interesting to compare the results obtained here with those published earlier by Strelow and Sondorp⁵ for gel resins of high capacity. Plotting their data by eqn. 3 gave pretty good results for some divalent metal ions, but the negative slopes for several trivalent metal ions were much lower than the expected value of 3.0 (see Table III).

Elution with divalent cations

Several metal cations were eluted with magnesium perchlorate eluents ranging from 10.0 to 0.50 mM. Capacity factors were calculated from the retention times and are shown in Table V. Plots of $\log k'$ against the log of magnesium ion concentration were linear in every case. For most of the metal ions the slope was close to -1.0 , which is the theoretical slope for a divalent metal eluted with a divalent metal ion.

Several divalent metal cations were eluted with eluents containing the ethylenediammonium or *m*-phenylenediammonium 2+ cation. Capacity factors for metal cations using 1.00 mM solutions (pH 2.5) of these cations as eluents are given in Table VI. Capacity factors for the other eluents are given for comparison. It can be seen that the two diamine eluents behave similarly. They are much more efficient than magnesium(II) eluents and eluents containing H^+ or Na^+ .

The early elution of copper(II) with the ethylenediammonium 2+ eluent as compared with the *m*-phenylenediammonium 2+ eluent is of some interest. Even at pH as low as 2.5 some complexation of the copper(II) by the ethylenediammonium eluent may be occurring.

TABLE V

CAPACITY FACTORS (k') FOR VARIOUS CATIONS USING MAGNESIUM PERCHLORATE ELUENTS AND SLOPE OF LINEAR REGRESSION, $\log k'$ versus $[Mg(ClO_4)_2]$

Cation	Magnesium concentration (mM)				Slope*
	10.0	5.0	1.0	0.50	
V(IV)	0.67	1.60	7.37	13.4	-0.99
Zn(II)	1.37	2.79	13.1	24.9	-0.93
Co(II)	1.56	3.09	14.2	25.4	-0.94
Fe(II)	1.43	3.03	13.6	26.1	-0.96
Ni(II)	1.45	3.09	14.0	26.7	-0.96
Cu(II)	1.92	3.66	15.8	26.7	-0.89
Zr(IV)	1.58	3.11	14.4	27.3	-0.95
Hg(II)	1.49	3.15	14.6	27.7	-0.97
Mn(II)	1.66	3.39	15.4	29.7	-0.96
Cd(II)	1.03	2.53	15.8	33.3	-0.86
U(VI)	2.79	5.90	22.0	38.2	-1.29
Pb(II)	13.1	31.9	—	—	—

* Correlation coefficient was 0.998 in every case.

TABLE VI

COMPARISON OF CAPACITY FACTORS (k') OF VARIOUS CATIONS WITH CATIONIC ELUENTS

Concentrations: HClO_4 , 0.250 M ; NaClO_4 , 0.100 M ; all others are 1.00 mM , pH 2.5 ($t_0 = 0.495$ min). EnH_2^+ = ethylenediamine eluent; PhenH_2^+ = *m*-phenylenediamine eluent.

Cation	Eluent				
	HClO_4	NaClO_4	EnH_2^+	PhenH_2^+	$\text{Mg}(\text{ClO}_4)_2$
Ba(II)	15.8	—	14.00	17.8	—
Be(II)	1.86	1.05	1.58	—	—
Ca(II)	5.98	4.36	4.81	5.21	—
Cd(II)	3.56	3.23	3.27	3.72	15.8
Co(I)	2.02	2.79	2.97	2.97	14.2
Cu(II)	3.19	2.79	2.46	3.54	15.8
Fe(II)	1.94	3.58	2.87	2.85	13.6
Hg(II)	2.00	2.95	2.77	3.15	14.6
Mg(II)	1.39	1.23	1.98	2.40	—
Mn(II)	2.02	3.45	3.01	3.01	15.4
Ni(II)	2.02	2.42	2.95	3.01	14.0
Pb(II)	28.5	27.7	19.8	24.2	—
Sr(II)	2.48	5.92	6.42	7.27	—
U(VI)	3.52	7.25	6.24	6.02	22.0
V(IV)	0.91	0.95	2.10	2.20	7.4
Zn(II)	2.55	2.20	2.75	2.91	13.1
Zr(IV)	2.00	2.71	2.85	3.09	14.4

Effect of resin capacity

The capacity factors for metal cations were measured with 0.75 M perchloric acid eluent on resins of 6.1, 13.8, and 24.9 $\mu\text{equiv./g}$ exchange capacity. The results, shown in Table VII, show a substantial increase in capacity factors with increased resin capacity. According to eqn. 3, the logarithm of k' should vary linearly with the logarithm of the resin capacity. Linear plots are indeed obtained with good linear regression correlation coefficients. However, the slopes are as much as two to three times lower than the theoretical values and the slopes vary from one metal ion to another.

An explanation of these observations might be that sulfonation of the resins proceeds inwardly from the outside of the resin beads. Thus, resins of higher capacity are apt to have thicker sulfonation layers. The microscopic selectivity coefficient may well change in various parts of the sulfonation layer. The selectivity coefficients measured would be an average of different microscopic values and might not follow the behavior predicted by eqn. 3.

Another factor to consider is that styrene moieties in the resin are more easily sulfonated than the divinylbenzene portions. This, along with the existence of a cross-linking gradient, will result in a capacity gradient radiating outward from the core of each resin bead. It has been shown that increased selectivity is observed with increasing the crosslinking of resins of the same total capacity¹¹. Higher distribution coefficients are obtained when the exchange groups are located more deeply in the

TABLE VII

CAPACITY FACTORS (k') FOR CATIONS WITH RESINS OF DIFFERENT BULK DENSITIESEluent is 0.75 *M* perchloric acid.

Cation	Resin capacity ($\mu\text{equiv./g}$)		
	6.1	13.8	24.9
V(IV)	0.12	0.40	0.81
Be(II)	0.24	0.32	0.38
Zr(IV)	0.24	0.40	1.03
Mg(II)	0.26	0.32	0.65
Fe(II)	0.26	0.40	0.93
Ni(II)	0.28	0.51	0.87
U(VI)	0.28	0.59	1.21
Mn(II)	0.28	0.67	1.27
Zn(II)	0.30	0.42	0.85
Cu(II)	0.32	0.46	0.95
Cd(II)	0.32	0.51	1.11
Ca(II)	0.57	1.05	2.46
Ba(II)	1.52	5.05	—
Pb(II)	1.90	4.97	11.05
Fe(III)	2.89	5.68	11.0
In(III)	3.05	6.12	—
Lu(III)	6.6	15.9	35.4
Yb(III)	7.2	16.4	36.8
Tm(III)	7.5	17.8	38.4
Er(III)	7.9	18.8	42.4
Y(III)	8.2	19.3	42.8
Ho(III)	8.6	20.4	46.9
Dy(III)	9.3	24.4	55.4
Tb(III)	10.6	26.7	65.0
Gd(III)	12.5	31.5	73.1
Eu(III)	13.8	35.4	84.2
Sm(III)	15.4	39.4	95.8
Nd(III)	17.8	45.0	106.3
Pr(III)	18.6	48.9	115.0
Ce(III)	21.2	56.6	124.6
La(III)	23.8	68.1	172.1
Bi(III)	—	42.4	122.6

resin beads. Variation of distribution coefficients at different depths within each bead may well account for excessive tailing of various cations, especially with resins of higher capacity.

Jěrábek¹² has shown that the pore size of natural gel resins varies with the depth into the resins. The results were explained primarily through swelling of the outer layers of the resin bead. Little emphasis was placed on the inhomogeneity of the beads themselves. Sulfonic acid groups cause a gel resin to swell even further and enhance the pore variations. Such swelling accentuates the differences in the exchange environment.

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