ION EXCHANGE PROCEDURES

I. CATION EXCHANGE IN CONCENTRATED HCl AND HClO₄ SOLUTIONS*

FREDERICK NELSON, TAKEO MURASE** AND KURT A. KRAUS

*Chemistry Division, Oak Ridge National Laboratory,
Oak Ridge, Tenn. (U.S.A.)*

Approximately three years ago systematic studies oriented toward development of a general ion exchange analysis scheme were initiated at this laboratory. While the ultimate objective has so far not been achieved, considerable new information has been accumulated and a variety of procedures developed, many of which are expected to be part of such a scheme. The purpose of the present series of papers is to present these procedures and other pertinent results as they are developed.

The studies were initiated because there seems to be an ever growing need for development of new comprehensive separations schemes by which any mixture of elements can rapidly and cleanly be separated into groups and individual components. Schemes for separation of elements based on precipitation methods (*e.g.*, the NOYES AND BRAY scheme) are, for most purposes. too slow or cumbersome and are usually not applied to specific problems without drastic modification. Further, separations based largely on precipitation methods normally require addition of carriers in tracer and other radiochemical work.

Schemes handling a variety of tracer mixtures have become of increasing importance in recent years in such fields as activation analysis, fission product analysis and in the isolation of specific radio-isotopes from targets. A number of methods have been developed, some with broad coverage of elements. However, it appears that a still more general scheme, adaptable to both tracer and macro concentrations and embracing essentially all elements, remains an important goal. One would hope that such a scheme might combine reasonable speed, theoretical and experimental simplicity, high product purity, good recovery of the elements, and adaptability to simultaneous multiple analysis without excessive labor.

Ion exchange techniques seem to meet most of these requirements. They can be operated with (carrier-free) tracer and macro quantities. They are applicable to essentially all the elements through proper choice of resins, media, oxidation–reduction and complexing reactions. The techniques are simple and intrinsically rapid, at least when short columns can be used at moderately rapid flow rates. Several columns can be operated simultaneously. Purity and yield of separated elements are usually high.

Ion exchange as a separations tool has been intensively studied for the last 20

years. A large body of basic information is available regarding the anion and cation exchange behavior of essentially all the elements. One might thus have expected that a new analysis scheme could be developed simply by properly arranging available information. However, from an examination of these data we concluded that insufficient information was available to permit development of a generalized scheme, applicable to (initial) samples containing any number of elements. In particular, it did not appear possible to specify, on the basis of existing information, a set of conditions under which elements could be separated into groups without overlapping.

As mentioned in a previous review[1] a gap existed in our knowledge of cation exchange of the elements at high ionic strength. Judging from the success of high ionic strength anion exchange, which during the last 10 years has become very popular, a thorough examination of high ionic strength cation exchange now seemed required.

There was reason to expect on the basis of a number of earlier publications[2-8] that such studies would be rewarding. DJURFELDT AND SAMUELSON[2] called attention to "anomalous" cation exchange behavior of iron in moderately concentrated HCl solutions; adsorbability did not decrease with increasing ionic strength as expected from simple mass action considerations—rather, there was significant adsorption of iron by cation exchangers from moderately concentrated HCl solutions. STREET, SEABORG AND DIAMOND[3-5] pointed out "anomalous" behavior in adsorbability studies of some rare earths and alkaline earths in HCl solutions. A few years ago, it was found in this laboratory[6] that strong adsorption on cation exchangers may occur from concentrated HCl solutions with some elements which exist substantially only as anionic complexes (of the type $MCl_4{}^-$) in the aqueous phase. Simultaneously with the work to be reported here and independently of it, CHOPPIN AND DINIUS[8] found very high adsorbabilities for a number of elements in perchloric acid solutions.

A rather broad survey of adsorbabilities of the elements in perchloric acid solutions has now been completed and the results are given in the present paper. These data are compared with adsorbabilities from HCl solutions which were obtained with the same ion exchange resin. The large differences in adsorbabilities of the elements in these two media at high ionic strength are striking and lead to many interesting separations. Through use of mixtures of these and other acids, many new techniques for separations become possible. A few of these will be mentioned here; the broad survey of high ionic strength separations in mixed acid systems, which were carried out at this laboratory, will be discussed in subsequent papers.

EXPERIMENTAL

1. Exchanger

A sulfonic acid–polystyrene–divinylbenzene resin of moderate cross linkage (Dowex 50-X4) was used. Originally, it was hoped that this resin might have reasonably rapid ion exchange rates even in concentrated electrolyte solutions. However, presumably because of the reduced water content of the resin in concentrated HCl and $HClO_4$ solutions, exchange rates in these media are unfavorable, although they are satisfactory at lower ionic strength. Because of these slow equilibration rates, very fine particles (270–325 mesh water-wet) were selected for column operation. On the basis of a number of preliminary experiments, still finer resins would give substantially improved performance in concentrated acids. For batch equilibrations, a somewhat coarser fraction (200–270 mesh) of the same resin was preferred.

The resin was screened, washed, and air dried for convenience in weighing. Moisture content and capacity were determined by standard methods (see e.g., KRAUS AND RARIDON[9]). Capacity was 5.12 equivalents per kg dry hydrogen form resin.

2. Procedure

Adsorbabilities were determined by column elution, preloaded column, and batch equilibration techniques[10]. They will be expressed as weight distribution coefficients, D (amount per kg dry resin/amount per liter of solution) or volume distribution coefficients, D_v (amount per liter of bed/amount per liter of solution); D is related to D_v by the relationship $D = D_v/\rho$, where ρ is the bed density in the medium of interest.

Bed densities were determined in HCl and $HClO_4$ solutions. Approximately 1 g samples of resin were placed in a graduated tube of 0.25 cm^2 cross-sectional area; the beds were treated with water or electrolyte solutions and the bed volumes measured. The results are summarized in Fig. 1 as plots of $1/\rho$ (l of bed/kg dry resin) versus
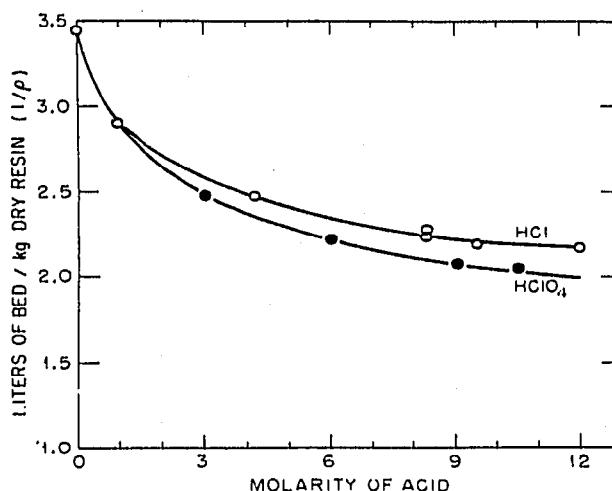

Fig. 1. Bed volume of Dowex 50-X4 in HCl and $HClO_4$ solutions.

molarity M (moles/l of solution) of acid. The resin shrinks greatly with increasing acid concentration from $1/\rho = 3.45$ l/kg in water to 2.18 and 2.00 l/kg in 12 M HCl and 12 M $HClO_4$ respectively.

For measurement of distribution coefficients by the column elution method, small aliquots of the solution containing the ions of interest were added to small columns (ca. 4 cm × 0.25 cm^2) of the resin pretreated with the appropriate HCl or $HClO_4$ solutions; the columns were eluted with the same acid solutions. Values of D_v were computed from the number of (geometric) column volumes (height × cross-sectional area) of effluent at which the metal appeared in maximum concentration; appropriate corrections were made for interstitial volume. As discussed earlier[10], this method is particularly suited when D_v is less than ca. 10.

For measurement of larger distribution coefficients, batch equilibration techniques were used. Weighed amounts of resin were agitated with known volumes of solution until there was no significant change in metal concentration with time. From analysis of the solution phase before and after equilibration, the weight distribution coefficients, D, were computed. Usually, 10 h equilibration was sufficient; however,

for the most concentrated acid solutions, agitation times of 2–3 days were sometimes required.

For measurement of very high distribution coefficients, the preloaded column technique was used (see also KRAUS, PHILLIPS AND NELSON[11]). A tracer of the element was first uniformly adsorbed on a weighted amount of resin; a column was prepared from the loaded resin and eluting solution passed through it. Distribution coefficients were computed from the tracer concentration in the effluent and its known concentration in the preloaded bed.

Distribution coefficients were usually determined at metal concentrations sufficiently low so that the capacity of the resin utilized for adsorption (loading) was less than 1 %. In some experiments with concentrated $HClO_4$ solutions and metals which form very strong chloride complexes, e.g., Ag(I), Hg(II), Bi(III), Tl(III), adsorption of tracers tended to be erratic presumably because trace amounts of chloride (ca. 10^{-4} M) initially present in the perchloric acid used strongly affect distribution coefficients. After adding the elements in sufficient excess (ca. 10^{-3} M) to override such effect, the results were reproducible. This caused substantially higher loading when adsorbability was high and distribution coefficients reported for some conditions thus refer to loading greater than 1 %.

Except when otherwise noted, the experiments were carried out at 25°. Temperature of the columns was controlled by jacketing them and pumping thermostated water through the jacket[12]. With the fine mesh resins used, gravity flow rates were usually too slow. Hence, the columns were operated under modest (< 2 p.s.i.) pressure.

3. Analytical methods

Most analyses were carried out radiometrically. Aliquots of solutions containing γ-emitters or energetic β-emitters were counted in a well-type scintillation counter, usually by integral counting techniques. When more than one tracer was present or in analyses of parent–daughter pairs, gamma spectrometry was used for identification and quantitation. Gamma energies were resolved with a 200 channel RIDL (Radiation Instrument Development Laboratory) Gamma Spectrometer, Model 34-8.

Alpha counting was used for analysis of radium, plutonium, curium and most americium samples. Aliquots of HCl and $HClO_4$ solutions were evaporated to dryness in small glass beakers, the residue taken up with hot 8 M HNO_3, transferred to stainless steel plates, evaporated and flamed before counting in an α-proportional counter. When necessary, pulse analysis techniques were used.

Aluminum analyses were carried out by spot testing with alizarin when the band elution method was used. Such semi-quantitative methods are satisfactory for determining D_v by establishing peak positions of the elution bands. In equilibration experiments, Al(III) concentrations were determined by EDTA titration with Eriochromeblack T as indicator. The samples were evaporated, the residue dissolved in 1 M HCl, excess EDTA added, and the mixture adjusted to pH 10 with ammonia. Back titration was carried out with standardized Zn(II) solution.

Several other elements were analyzed only semi-quantitatively when the band elution method was used: lithium and boron (borate) were analyzed by flame testing the effluent fractions; HNO_3, by noting appearance of brown fumes on warming the effluent samples with concentrated HCl; HF, by precipitation of LaF_3 on addition of $La(NO_3)_3$ solution; chloride, by precipitation of AgCl with $AgNO_3$; H_2SO_4, by pre-

cipitation of $BaSO_4$ on addition of $Ba(NO_3)_2$ solution. Adsorbability (D_v) of Cr(VI) and V(V), which in HCl and $HClO_4$ solutions tend to reduce, was determined by visually estimating the rate at which their bands (colored) moved down the column. The stock solutions were prepared immediately before use by dissolving CrO_3 or NH_4VO_3 in the appropriate acids.

In a number of column separations, millimolar rather than tracer concentrations of the elements were used. Pertinent details of solution preparation and analytical methods are given in the discussion.

4. Radioactive tracers

A list of the tracers used is shown in Table I. Most of the tracers were obtained from the Isotopes Division of Oak Ridge National Laboratory. The tracers, [7]Be, [22]Na, [28]Mg,

TABLE I

RADIOISOTOPES USED IN STUDY

Atomic No.	Isotope	Half-life*		Atomic No.	Isotope	Half-life*		Atomic No.	Isotope	Half-life*
4	^{7}Be	53	d	37	^{86}Rb	18.7	d	71	^{177}Lu	6.8	d
11	^{22}Na	2.6	y	38	^{85}Sr	64	d	72	^{181}Hf	43	d
	^{24}Na	15	h	39	^{91}Y	59	d	73	^{182}Ta	115	d
12	^{28}Mg	21.3	h	40	^{95}Zr	65	d	74	^{187}W	24	h
14	^{31}Si	2.62	h	41	^{95}Nb	35	d	75	^{186}Re	90	h
15	^{32}P	14.3	d	42	^{99}Mo	66	h	76	^{191}Os	15	d
19	^{42}K	12.4	h	43	^{99m}Tc	6	h	77	^{192}Ir	74	d
20	^{47}Ca	4.5	d	44	^{103}Ru	40	d	78	^{191}Pt	3.0	d
21	^{44}Sc	4.0	h		^{106}Ru	1.0	y		^{197}Pt	20	h
	^{46}Sc	84	d	45	^{102}Rh	206	d	79	^{198}Au	64.8	h
	^{47}Sc	3.4	d	46	^{109}Pd	13.6	h	80	^{203}Hg	47	d
22	^{44}Ti	10^3	y	47	^{110m}Ag	249	d	81	^{204}Tl	3.9	y
23	^{48}V	16.1	d		^{111}Ag	7.6	d	82	^{210}Pb	21	y
24	^{51}Cr	27.8	d	48	^{115m}Cd	43	d	83	^{207}Bi	30	y
25	^{54}Mn	314	d	49	^{114m}In	50	d		^{210}Bi	5	d
	^{56}Mn	2.58	h	50	^{113}Sn	118	d	84	^{210}Po	138.4	d
26	^{59}Fe	45	d	51	^{124}Sb	60	d	88	^{226}Ra	1620	y
27	^{60}Co	5.27	y		^{125}Sb	2.7	y	90	^{234}Th	24.1	d
28	^{65}Ni	2.56	h	52	^{123m}Te	104	d	91	^{233}Pa	27.4	d
29	^{64}Cu	12.9	h	53	^{131}I	8.05	d	92	^{237}U	6.75	d
30	^{65}Zn	245	d	55	^{134}Cs	2.1	y	93	^{238}Np	2.1	d
31	^{72}Ga	14.1	h		^{137}Cs	30	y		^{239}Np	2.35	d
32	^{77}Ge	11	h	56	^{133}Ba	7.5	y	94	^{239}Pu	$2.44 \cdot 10^4$	y
33	^{76}As	25.5	h	57	^{140}La	40.2	h	95	^{241}Am	458	y
	^{77}As	39	h	58	^{141}Ce	32.5	d	96	^{244}Cm	17.6	y
34	^{75}Se	120	d	63	^{155}Eu	1.7	y				
35	^{82}Br	35.7	h	70	^{169}Yb	32	d				

* From *Chart of the Nuclides*, Knolls Atomic Power Laboratory, December, 1961

[44]Ti–[44]Sc, [48]V, [54]Mn, [102]Rh and [191]Pt, which are prepared by cyclotron irradiation, were purchased* as radiochemically pure stock solutions or prepared by the Electronuclear Research Division with the ORNL 86-Inch Cyclotron.

* [7]Be, [22]Na, [44]Ti–[44]Sc, [54]Mn: Nuclear Science and Engineering Corporation, Pittsburgh, Pa.; [28]Mg: Brookhaven National Laboratory.

Short-lived tracers and others not routinely available from the Isotopes Division were prepared by neutron irradiation of appropriate target materials in the Low Intensity Training Reactor (LITR) or the Oak Ridge Research Reactor (ORR) at fluxes between 10^{12} and 10^{14} neutrons/cm²/sec.

Most tracers were initially in HCl or HNO_3 solutions; $HClO_4$ "stock" solutions were prepared from these by fuming with concentrated $HClO_4$.

5. *Purification of tracers*

Most tracers were of sufficient radiochemical purity to be used directly. When this was not the case, they were usually purified by "standard" ion exchange techniques. Some (non-standard) purification procedures are given below.

The [48]V tracer, prepared by proton irradiation of TiO_2, was separated and purified by cation exchange in HCl–HF as described earlier[13].

[191]Pt, obtained by proton irradiation of Ir metal was separated and purified by anion exchange after converting the target to soluble Ir(IV) and Pt(IV) chlorides by fusion in NaCl in an atmosphere of chlorine gas. The NaCl melt was dissolved in 1 M HCl and shaken with Ag metal to reduce Ir(IV) to Ir(III). The solution was passed into a small column of Dowex 1-X10 anion exchange resin. The column was washed with several column volumes of 6 M HCl containing Fe(II). Under these conditions, Ir(III) is eluted, while the [191]Pt remains adsorbed[14], presumably as the Pt(II) complex. Removal of [191]Pt was effected with *ca.* 8 column volumes of 11 M HCl at 50°. The effluent was evaporated with hydrogen peroxide to oxidize Fe(II) to Fe(III), adjusted to *ca.* 0.5 M HCl by water addition and passed into a small column of Dowex 50-X10 to remove Fe(III). On washing the column with 0.5 M HCl, [191]Pt appeared in the effluent while Fe(III) remained adsorbed.

The [226]Ra tracer* contained its decay products, primarily Rn, Po, Pb and Bi. The impurities were removed immediately before use by passing a 2 M HCl solution of the tracer through small columns of Dowex-1 anion exchange resin[15].

[234]Th was isolated from natural uranium by a method similar to that described by DYRSSEN[16]. Approximately 400 g of uranium nitrate hexahydrate were dissolved in 0.1 M HNO_3. The solution was passed through a 1.8 cm² × 5 cm (10 c.c.) bed of Dowex 50-X8 which strongly adsorbs Th(IV) under these conditions and concentrates it together with some uranium. Most of the uranium was selectively eluted with 4 M HCl after which Th(IV) was removed with 6 M HCl–1 M HF. The Th(IV) fraction was evaporated to near dryness, taken up in 12 M HCl and passed through a small bed of Dowex-1 anion exchanger to remove the last traces of U(VI).

Uranium analyses were carried out with [237]U rather than the more commonly available α-emitting isotopes in order to substitute more convenient γ-counting for tedious α-counting. The [237]U tracer was prepared by neutron irradiation of enriched [236]U. Since the preparation contained some [235]U and [238]U, separation of [237]U from fission products and [239]Np was required. The separation method, which will be described in detail in a separate publication[17] makes use of the strong adsorption of U(VI) by cation exchangers from $HClO_4$ media (see also Section 2 of RESULTS AND DISCUSSION). Final purification of [237]U was carried out by anion exchange in HCl using a modification of the procedure of CROUCH AND COOK[18].

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* We are indebted to Dr. P. S. RUDOLPH of the ORNL Chemistry Division for this tracer.

RESULTS AND DISCUSSION

1. *Adsorbabilities in 9 M HCl and 9 M HClO₄*

To evaluate rapidly some of the significant aspects of cation exchange at high ionic strength, μ, one may examine adsorbabilities in 9 M HClO₄ and 9 M HCl solutions. The corresponding distribution coefficients are given in Table II; values of D_v are tabulated because of their direct relationship to elution band maxima, c.v.$_{max}$, expressed as (geometric) column volumes ($D_v + i = $ c.v.$_{max}$, where $i \approx 0.4$ is the fractional interstitial volume).

Table II gives information on most of the elements. A few relatively volatile or, highly insoluble elements were not studied. Some elements which hydrolyze and precipitate in perchloric acid or which are normally handled as chloride complexes, were studied only in HCl solutions. Inclusion of these elements (as well as some of the elements listed) in a separations scheme based on the use of HClO₄ requires presence of appropriate complexing agents to assure reproducibility of properties, *i.e.*, they should be handled in acid mixtures.

From a cursory examination of Table II, a number of striking features concerning cation exchange at high ionic strength becomes apparent:

(i) A large number of elements show at least moderate adsorbabilities ($D_v > 1$) in either 9 M HCl or 9 M HClO₄. Thus a large number of high ionic strength cation exchange separations are feasible.

(ii) Adsorbabilities are usually substantially larger in 9 M HClO₄ than in 9 M HCl. The principal exceptions are Fe(III), Ga(III), and presumably also Au(III). These are the elements which form complexes of the type MCl_4^-, whose special adsorption characteristics on cation exchangers were discussed earlier[6]. In addition, Sb(V) also shows very high adsorption from 9 M HCl; its adsorbability seems to be very much higher than reported earlier[6]. D_v of Tl(III) in HCl is also somewhat greater than in HClO₄ as is D_v of Ra(II).

(iii) In 9 M HCl only 6 elements were found to have $D_v > 10$ (Au(III), Fe(III), Ga(III), Sb(V), Sc(III), Th(IV)). Most of these have $D_v > 100$; Sc(III) and Th(IV) have $10 < D_v < 100$.

(iv) In 9 M HClO₄ a large number of elements have $D_v > 10$. This large group of elements includes the rare earths, Sc(III), Y(III) and, interestingly, all the actinides. It also includes some alkaline earths: Ca(II), Sr(II); other divalent ions: Mn(II), Cd(II), Pb(II); trivalent ions: Fe(III), Ga(III), Bi(III); tetravalent ions: Ti(IV), Zr(IV), Hf(IV), V(IV); and ions of oxidation number five: V(V), Nb(V), Ta(V), Pa(V); and six: Cr(VI), Mo(VI), W(VI), U(VI). For most of these elements, D_v is larger than 100.

(v) The large differences in adsorbabilities of many elements in these media make high ionic strength solutions attractive for separations and isolations. A few such applications will be described below. However, the number of such examples has been intentionally kept small since it appears that the full benefits of high ionic strength cation exchange can best be developed through use of mixtures of these and other acids; properties of these mixtures will be discussed in subsequent publications.

2. *Some characteristics of cation exchange at high ionic strength*

(a) *Distribution coefficients.* The differences in intrinsic adsorbabilities of the various

TABLE II

DISTRIBUTION COEFFICIENTS IN 9 M HCl AND 9 M HClO$_4$

Element	D_v		Element	D_v	
	9 M HCl	9 M HClO$_4$		9 M HCl	9 M HClO$_4$
Ac(III)	~ 10*		Os(IV)	< 1	
Ag(I)	< 1	2.4			
Al(III)	0.6	3.8	P(H$_3$PO$_4$)	< 1	1
Am(III)	1.2	2.0·10^3	Pa(V)	< 1	> 1·10^3
As(III)	< 1	0.4	Pb(II)	< 0.5	< 1.9·10^1
As(V)	< 1	1.4	Pd(II)	< 1	
Au(III)	1.2·10^2		Po(IV)	< 1	< 1
			Pt(IV)	< 1	
B(H$_3$BO$_3$)	< 1	1	Pu(VI)	< 1	> 1·10^2
Ba(II)	4.5	4.9			
Be(II)	0.3	1.3	R.E.(III)		
Bi(III)	< 1	8.6·10^2	La(III)	4.5	3.3·10^3
Br(Br$^-$)	< 1	< 1	Eu(III)		2.0·10^3
			Yb(III)	1.0	1.3·10^2
Ca(II)	3.2	1.4·10^2	Lu(III)	0.8	8.7·10^1
Cd(II)	< 1	1.7·10^1	Ra(II)	2.5	2.0
Cl(Cl$^-$)	< 1	< 1	Rb(I)	< 1	< 0.5
Cm(III)	1	> 1·10^3	Re(VII)	< 0.8	< 1
Co(II)	0.3	1.5	Rh(III)	< 1	
Cr(III)	< 1	3.5	Ru(IV)	< 1	
Cr(VI)	< 1	> 1.0·10^2			
Cs(I)	< 1	0.6	S(HSO$_4$$^-$)	< 1	1
Cu(II)	0.4	1.2	Sb(III)	< 1	1
			Sb(V)	2·10^3	
F(F$^-$)	< 1	< 1	Sc(III)	1.7·10^1	7.2·10^5
Fe(III)	3·10^2	1.8·10^1	Se(IV)	< 1	0.7
Fr(I)	< 1*	< 1*	Sn(IV)	< 1	
			Sr(II)	3.5	2.9·10^1
Ga(III)	3.3·10^2	1.3·10^1			
			Ta(V)	1	> 1·10^3
Hf(IV)	< 1	9.6·10^2	Tc(VII)	< 0.5	< 1
Hg(II)	< 1	7	Te(IV)	< 1	2.8
			Th(IV)	2.8·10^1	> 1·10^7
I(I$^-$)	< 1	< 1	Ti(IV)	1	1.9·10^3
In(III)	< 1	9.5	Tl(III)	5.3	1
Ir(III)	< 1				
Ir(IV)	< 1		U(VI)	0.5	3.8·10^3
K(I)	< 1	0.3	V(IV)	< 1	2.1·10^1
			V(V)	2	> 1·10^2
Li(I)	< 1	0.5			
			W(VI)	< 1	> 5·10^2
Mg(II)	0.3	1.9			
Mn(II)	0.4	1.9·10^1	Y(III)	1.6	5.8·10^2
Mo(VI)	< 1	8.7·10^2			
			Zn(II)	< 1	1.8
N(NO$_3$$^-$)	< 1	1.5	Zr(IV)	1	2.1·10^3
Na(I)	< 1	< 0.5			
Nb(V)	1.6	> 1·10^3			
Ni(II)	< 1	1.0			
Np(VI)	< 1	> 1.0·10^2			

* Estimated.

elements, as characterized by the distribution coefficients at low ionic strength, μ, under non-complexing conditions, while significant and of principal interest in earlier ion exchange studies do not concern us here since the differences at high μ are often very much larger. For example, adsorbabilities of the alkaline earths at low μ vary substantially less than a factor of 10 and in a regular manner in the series Be(II) to Ra(II), with Ra(II) most strongly adsorbed[5,10]; in 9 M HClO$_4$ adsorbabilities differ by more than a factor of 100 and Ca(II) is most strongly adsorbed.

In addition to inversions of elution order, other striking departures from "ideal" on exchange behavior may occur at high μ, as illustrated in Fig. 2 with Sc(III).
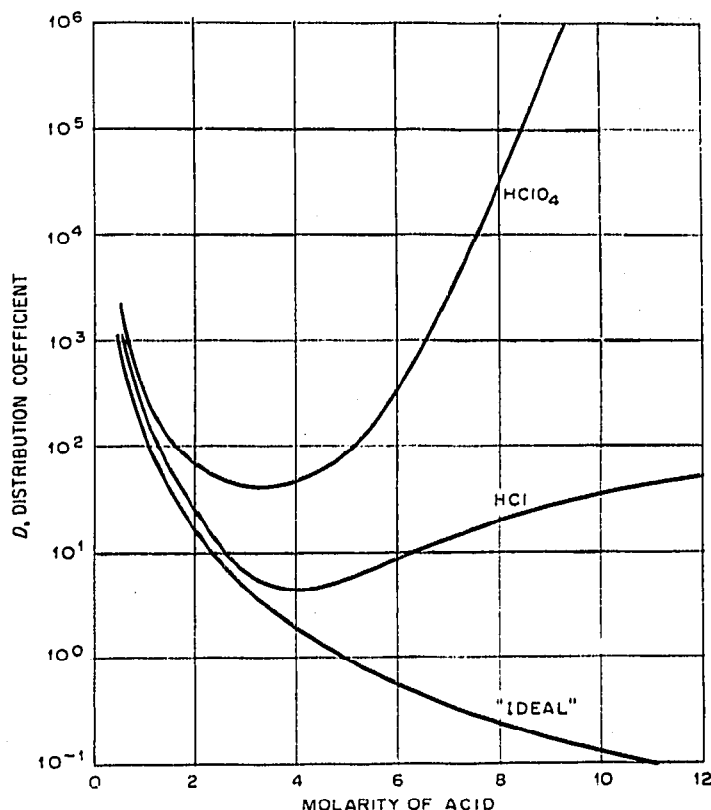
Fig. 2. Non-ideality at high ionic strength (Sc(III), Dowex 50-X4, 25°).

Its adsorption functions in HCl and HClO$_4$ are compared with an "ideal" function computed from the equilibrium expression for the exchange of the ions M^{+v} and B$^+$ with the assumptions (1) that M^{+v} is a trace ion, (2) that there is no invasion of the resin, and (3) that the appropriate activity coefficient ratio is constant.

The equilibrium expression for the exchange reaction, using the same standard states in both phases, is:

$$\frac{m_{M(r)}m_{B}{}^{v}}{m_{M}m_{B}{}^{v}{}_{(r)}}\,\frac{\gamma_{M(r)}\gamma_{B}{}^{v}}{\gamma_{M}\gamma_{B}{}^{v}{}_{(r)}} = 1 \tag{1}$$

where m is the concentration, γ the activity coefficient and subscript (r) designates the resin phase. (For discussion of the more general case of exchange with an ion B^{+b} see KRAUS AND NELSON[20]). After setting:

$$D_{M} = \frac{m_{M(r)}}{m_{M}} \text{ and } \Gamma_{M/B} = \frac{\gamma_{M(r)}\gamma_{B}{}^{\nu}}{\gamma_{M}\gamma_{B}{}^{\nu}{}_{(r)}} = \frac{\gamma_{\pm}{}^{\nu+1}{}_{MX_{\nu}(r)}\ \gamma_{\pm}{}^{2\nu}{}_{BX}}{\gamma_{\pm}{}^{\nu+1}{}_{MX_{\nu}}\ \gamma_{\pm}{}^{2\nu}{}_{BX(r)}}$$

eqn. (1) becomes:

$$\log D_{M} = -\nu \log m_{B} + \nu \log m_{B(r)} - \log \Gamma_{M/B} \tag{2}$$

and

$$\frac{\mathrm{d} \log D_{M}}{\mathrm{d} \log m_{B}} = -\nu + \nu \frac{\mathrm{d} \log m_{B(r)}}{\mathrm{d} \log m_{B}} - \frac{\mathrm{d} \log \Gamma_{M/B}}{\mathrm{d} \log m_{B}} \tag{3}$$

The limiting "ideal" conditions ($\Gamma =$ constant, $m_{B(r)} \approx$ constant, $m_{M(r)} \ll m_{B(r)}$) are equivalent to the simplifications:

$$\log D_{M} = -\nu \log m_{B} + \text{const.} \tag{2a}$$

and

$$\frac{\mathrm{d} \log D_{M}}{\mathrm{d} \log m_{B}} = -\nu \tag{3a}$$

The "ideal" curve of Fig. 2 was calculated on the basis of these assumptions with $\nu = 3$ after matching distribution coefficients at low μ; it, of course, does not show the minima and rapid rises of D with m which Sc(III) and many other elements show at high μ. Such positive slopes can only arise if d log Γ/d log m_{B} (eqn. (3)) is sufficiently negative since the resin invasion term d log $m_{B(r)}$/d log m_{B} is unlikely to become larger than unity.

Consideration of these non-ideality effects and estimation of their magnitude at high μ is simplified if one considers distribution of the components MX_{ν} and BX individually[21]. Using the same standard states in both phases, the conditions of equilibrium are:

$$a_{MX_{\nu}} = a_{MX_{\nu}(r)} \tag{4}$$

$$a_{BX} = a_{BX(r)} \tag{4a}$$

where a is the activity.
From eqn. (4):

$$D_{M} = \frac{m_{M(r)}}{m_{M}} = \frac{m_{X}{}^{\nu}\ \gamma_{\pm}{}^{\nu+1}{}_{MX_{\nu}}}{m_{X(r)}{}^{\nu}\ \gamma_{\pm}{}^{\nu+1}{}_{MX_{\nu}(r)}} \tag{5}$$

or:

$$\frac{\mathrm{d} \log D_{M}}{\mathrm{d} \log m_{X}} = \nu \left(1 - \frac{\mathrm{d} \log m_{X(r)}}{\mathrm{d} \log m_{X}} \right) - (\nu + 1) \frac{\mathrm{d} \log \Gamma_{MX_{\nu}}}{\mathrm{d} \log m_{X}} \tag{5a}$$

where $\Gamma_{MX_{\nu}} = \gamma_{\pm\ MX_{\nu}(r)}/\gamma_{\pm\ MX_{\nu}}$. The terms $m_{X}{}^{\nu}/m_{X(r)}{}^{\nu}$ or d log $m_{X(r)}$/d log m_{X} can readily be estimated if $m_{M} \ll m_{X}$ and $m_{M(r)} \ll m_{B(r)}$ since then $m_{X} \approx m_{BX}$, $m_{B(r)} \approx C + m_{X(r)}$, where C is the capacity. These simplifications together with eqn. (4a) lead to:

$$\frac{\mathrm{d} \log m_{X(r)}}{\mathrm{d} \log m_{X}} = \frac{\mathrm{d} \log m_{BX(r)}}{\mathrm{d} \log m_{BX}} = 2 - \frac{\mathrm{d} \log m_{B(r)}}{\mathrm{d} \log m_{BX}} - 2 \frac{\mathrm{d} \log \Gamma_{BX}}{\mathrm{d} \log m_{BX}} \tag{5b}$$

When $\Gamma_{MX_{\nu}}$ and $\Gamma_{BX} = \gamma_{\pm\ BX(r)}/\gamma_{\pm\ BX}$ are substantially constant, and when $m_{B(r)} \approx C$, eqns. (5) yield d log D_{M}/d log $m_{BX} \approx -\nu$, as did eqn. (1) under similar assumptions.

At high electrolyte concentrations these simplifications do not hold; instead $m_{BX(r)} \approx m_{BX}$ and $d \log m_{BX(r)}/d \log m_{BX} \approx 1$, provided concentrations are expressed in moles/1000 g water in both phases. This, at least, was the case with a number of simple electrolytes in anion exchangers[21]. It presumably is also a good approximation for describing the invasion of cation exchangers by simple electrolytes as indicated by recent measurements of CHOPPIN AND DINIUS[22] on invasion of Dowex 50-X4 by perchloric acid.

Eqn. (4) then becomes:

$$D_M \approx \frac{\gamma_{\pm MX_\nu}^{\nu+1}}{\gamma_{\pm MX_\nu(r)}^{\nu+1}} = \frac{1}{\Gamma_{MX_\nu}^{\nu+1}} \tag{6}$$

and

$$\frac{d \log D_M}{d m_{BX}} \approx (\nu+1)\left[\frac{d \log \gamma_{\pm MX_\nu}}{d m_{BX}} - \frac{d \log \gamma_{\pm MX_\nu(r)}}{d m_{BX}}\right] = -(\nu+1)\frac{d \log \Gamma_{MX_\nu}}{d m_{BX}} \tag{6a}$$

Thus, distribution coefficients at high μ are determined largely by the activity coefficient ratio Γ_{MX_ν}. If this ratio were near unity, as it appears to be for the supporting electrolyte, no unusual adsorption effects should occur at high μ even if the individual activity coefficients are much larger than unity. As seen from Table II, this condition seems to apply for a surprisingly large number of elements. However, for Sc(III) and the many other elements which show considerable adsorption, particularly in concentrated perchloric acid solutions, Γ_{MX_ν} must be considerably smaller than unity; of course, the distribution coefficient is given by the $(\nu+1)$ power of this ratio. Examination of the distribution functions of these adsorbable elements shows an approximately linear increase of $\log D$ with m_{HClO_4} after D has gone through the minimum. This is not surprising since it is reasonable to expect that (eqn. (6a)) both $\log \gamma_{\pm MX_\nu}$ and $\log \gamma_{\pm MX_\nu(r)}$ vary linearly with m_{HClO_4}.

More detailed quantitative comparisons and evaluation of $\gamma_{\pm MX_\nu(r)}$, which is required for a deeper understanding of the phenomena, seem impossible at present. Not only is accurate information lacking on electrolyte invasion of the resin used here and its water content (note that concentrations in the resin should be expressed as moles/kg water) but the pertinent activity coefficients for the aqueous phase are also not available. Needed are the values of $\gamma_\pm$ of the trace components (MX_ν) in the supporting electrolyte ($HClO_4$ or HCl). Some qualitative information, however, can be obtained by comparison of the distribution coefficients in 9 M $HClO_4$ (14.5 molal) of a series of divalent ions for which the·activity coefficients of the perchlorates in their two component (water–salt) systems are known[23] at the same ionic strength.

Fig. 3 gives such a comparison for Ba, Pb, Sr, Ca, Mg, Zn, and UO_2^{2+}; for their perchlorate salts ($\mu = 14.5$) $\gamma_\pm$ is estimated to be 2.10, 3.75, 9.1, 23.5, 103, 117 and 610, respectively. Most of the points fall reasonably well on a straight line; it can be described by the relationship $\log D_M \approx 0.40 + 1.155 \log \gamma_{\pm MX_2(m = 4.8)}$.

Probably the most striking feature of Fig. 3 is the fact that Zn(II) and Mg(II) which have very high values of $\gamma_\pm$, have distribution coefficients $D = ca.$ 4; from the line defined by the other salts $D \approx 500$ would have been predicted. We have no explanation for these large apparent differences in the interactions of these salts with the ion exchangers which lead to such large differences in selectivity at high ionic
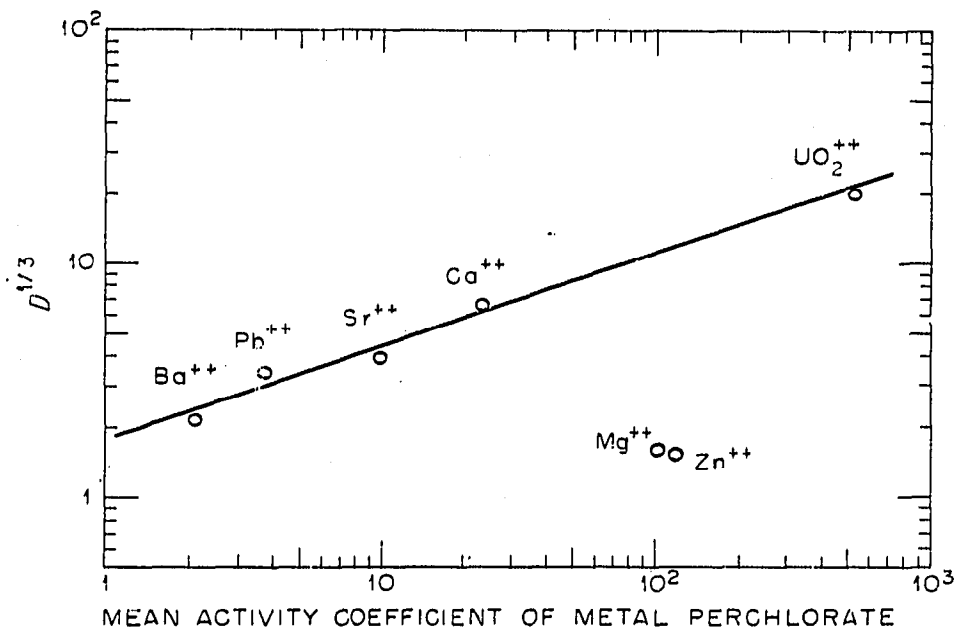
Fig. 3. Adsorption of trace metals from $HClO_4$ solution (9 M $HClO_4$, Dowex 50-X4, 25°).

strength. In a previous paper[6] in which the unusually high adsorption of some complex anions by cation exchangers was discussed, we proposed that these probably interact with the resin network. For the adsorbable cations in perchlorate solutions one might propose interaction (complex formation?) with the sulfonate groups of the exchangers. But even such a hypothesis leaves unresolved the question as to why this interaction should be so specific nor can it be readily reconciled with our observations (see next section) that distribution coefficients vary in an essentially ideal manner over a wide range of loading conditions.

(b) *Loading effects*. To allow direct comparison of observed distribution coefficients, most adsorption data were obtained under conditions of low loading, L, defined as:

$$L = \frac{vm_{M(r)}}{C_{(r)}} \tag{7}$$

where $C_{(r)}$ is the resin capacity expressed in the same concentration units as $m_{M(r)}$. With the tracer techniques used, loading of the high capacity exchanger (5.12 equivalents/kg dry resin) was generally less than $L = 0.01$. To establish that the unusually high adsorbabilities exhibited by some elements in concentrated electrolyte solutions were not anomalous "tracer" effects, a variety of "loading" experiments was carried out.

Two typical break-through experiments are illustrated in Fig. 4. For the first, a 9.2 M $HClO_4$ solution containing 0.1 M Ce(III) (with [144]Ce) was passed into a 0.25 cm² × 4 cm column of Dowex 50-X4 at 50° at a flow rate of 0.2 cm/min. No significant Ce(III) break-through occurred during the first 6 column volumes (c.v.); the 50 % break-through point (where the concentration of Ce(III) in the effluent is half its concentration in the feed) occurred at 7.7 c.v. This corresponds (after correcting for interstitial volume) to a total uptake of 0.73 moles of Ce(III)/l of bed. Since the ex-
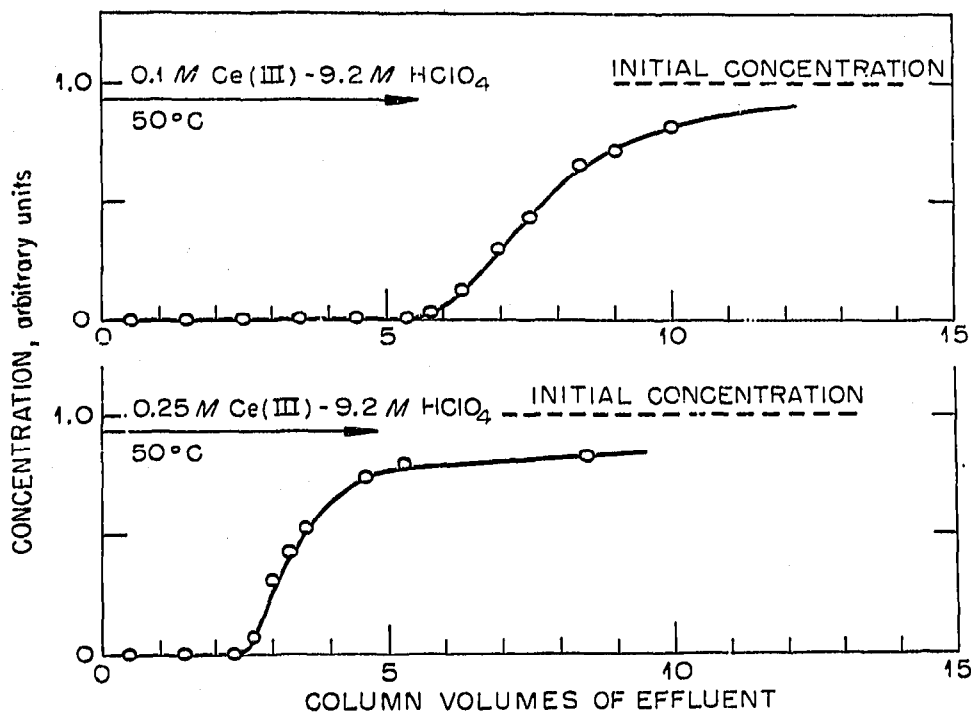
Fig. 4. Adsorption of Ce(III) from $HClO_4$ solution (Dowex 50-X4, —400 mesh, 25°).
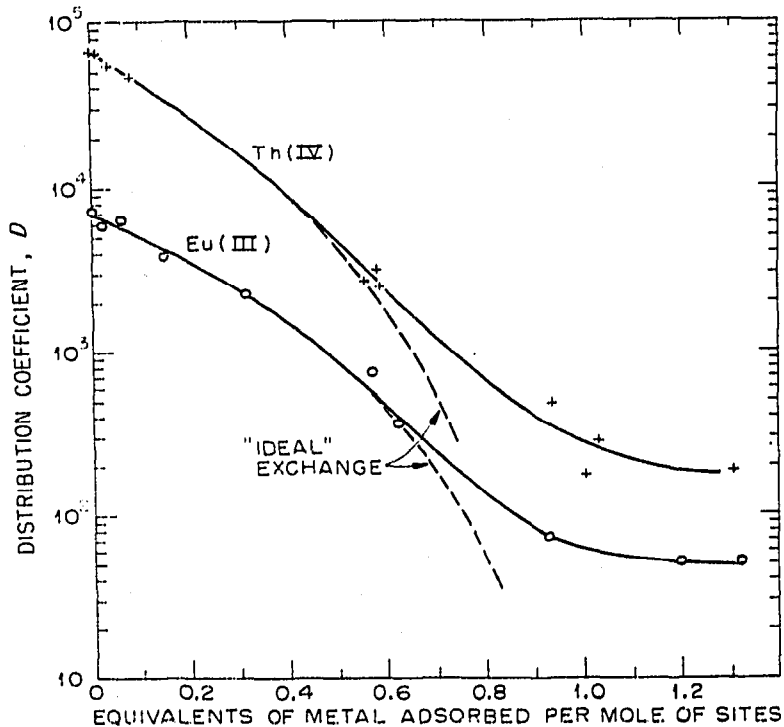
Fig. 5. Effect of loading on adsorbability (Dowex 50-X4, 25°). O—O Eu(III) in 9.2 M $HClO_4$; +—+ Th(IV) in 6.0 M $HClO_4$.

change capacity was 2.47 equivalents/l of bed, this corresponds to 89 % loading of the column (L = 0.89).

In the second example, a 0.25 M Ce(III) solution (with [144]Ce) in 9.2 M HClO$_4$ was passed through a small column under similar conditions; 50% break-through occurred at 3.6 c.v., corresponding to an uptake of 0.8 moles/l of bed, or L = $ca.$ 0.97. In neither experiment were the break-through curves symmetrical; beyond 50 % break-through the effluent concentration slowly approached the feed concentration. The exchange rates became increasingly unfavorable as the columns became heavily loaded. Nevertheless, high utilization of the columns can be achieved at moderate flow rates.

In more detailed studies of loading effects, measurements were carried out with Eu(III) in 9.1 M HClO$_4$ and Th(IV) in 6.0 M HClO$_4$*. The batch equilibration method was used; different loadings were obtained through control of the initial metal concentration and the ratio of solution volume to resin weight. Loading, L, was computed according to eqn. (7) with v = 3 for Eu(III) and v = 4 for Th(IV).

A plot of log D $versus$ L is shown in Fig. 5. At low loading (L < 0.01) D was essentially independent of L, as expected. Between 5 and 75 % loading, D falls off rapidly; at still higher loading, D decreases only slowly. Values of L significantly larger than unity can be reached with $D \gg 1$.

The shape of the loading curve is given by the derivative either of eqn. (1) or eqn. (5):

$$\frac{1}{v}\frac{d \ln D'_M}{dL} = \frac{d \ln m'_{B(r)}}{dL} - \frac{d \ln m_B}{dL} + \frac{v-1}{v}\frac{d \ln f}{dL} - \frac{1}{v}\frac{d \ln \Gamma_{M/B}}{dL} \tag{8}$$

$$\frac{1}{v}\frac{d \ln D'_M}{dL} = -\frac{d \ln m'_{X(r)}}{dL} + \frac{d \ln m_X}{dL} - \frac{v+1}{v}\frac{d \ln f\Gamma_{MX_v}}{dL} \tag{9}$$

For eqns. (8) and (9) and the rest of this section we shall distinguish between resin concentrations expressed as moles/kg dry resin (primed quantities) and moles/kg water in the resin (unprimed quantities); the relation between these two concentration units is m = $m'f$ where $1/f$ is the water content (kg water/kg dry resin).

We may define an ideal loading curve as one for which the water content, the activity coefficient ratios and the concentration of the supporting electrolyte are constant and where $m'_{B(r)}$ = C' — $vm'_{M(r)}$ = $C'(1 - L)$. This leads to:

$$\frac{d \log D'_M}{dL} = -\frac{v}{2.303(1-L)} \tag{8a}$$

The curves of Fig. 5 marked "ideal" are drawn on the basis of these simplifications. Agreement between observed and calculated curves is surprisingly good for both Eu(III) and Th(IV) up to L = $ca.$ 0.6 in spite of the fact that because of electrolyte invasion $m'_{B(r)}$ > (C' — $vm'_{M(r)}$). Further, under the conditions of these experiments, d ln $\Gamma_{M/B}$ and d ln f almost certainly are not zero.

Indeed, adherance of even the initial loading curve (near L = 0) to the highly

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* The Th(IV) loading experiments were carried out by Dr. E. L. Lind, Central Washington State College, Ellensburg, Washington, ORINS Research Participant at ORNL, 1962–1963. We are indebted to Dr. Lind for permission to quote these results.

restrictive "ideal" conditions is very difficult to understand at high μ. Thus, in addition to the equilibrium equation for the distribution of the components BX and MX_{ν}, the electro-neutrality restriction:

$$\nu m'_{M(r)} + m'_{B(r)} = C' + m'_{X(r)} \tag{10}$$

or its equivalent:

$$(1 - L) = \frac{1}{C'}\left(m'_{B(r)} - m'_{X(r)}\right) \tag{11}$$

must apply. If we evaluate d ln $m'_{B(r)}/dL$ from eqn. (10), eqn. (8) becomes:

$$\frac{1}{\nu}\frac{d \ln D'_M}{dL} = \frac{C'}{m'_{B(r)}}\left[\frac{dm'_{X(r)}}{\nu dm'_{M(r)}} - 1\right] - \frac{d \ln m_B}{dL} + \frac{\nu - 1}{\nu}\frac{d \ln f}{dL} - \frac{1}{\nu}\frac{d \ln \Gamma_{M/B}}{dL} \tag{12}$$

If we further make the assumptions, justifiable at high values of D'_M, that m_B, m_X, $\gamma_{\pm BX}$ and $\gamma_{\pm MX_{\nu}}$ in the aqueous phase are independent of L, eqn. (12) becomes:

$$\frac{1}{\nu}\frac{d \ln D'_M}{dL} = \frac{C'}{m'_{B(r)}}\left[\frac{dm'_{X(r)}}{\nu dm'_{M(r)}} - 1\right] + \frac{\nu - 1}{\nu}\frac{d \ln f}{dL} - \frac{\nu + 1}{\nu}\frac{d \ln \gamma_{\pm MX_{\nu}(r)}}{dL} + \frac{d \ln \gamma_{\pm BX(r)}}{2 \, dL} \tag{12a}$$

This clearly reduces to eqn. (8a) if there is no invasion ($dm'_{X(r)} = 0$) and if d ln $f =$ d ln $\gamma_{\pm MX_{\nu}(r)} =$ d ln $\gamma_{\pm BX(r)} = 0$. However at finite invasion the simultaneous assumptions that d $m'_{X(r)}/\nu$ d $m'_{M(r)} = 0$, d ln f/d $L = 0$ and that the activity coefficient derivatives are zero lead to a logical inconsistency. Thus, with d $m'_{X(r)}/\nu$ d $m'_{M(r)} = 0$ electro-neutrality requires d $m'_{B(r)}/\nu$ d $m'_{M(r)} = -1$. Since we assumed operation at constant activity of BX, invariance of $m'_{X(r)}$ can be reconciled with a decrease in $m'_{B(r)}$ only if $\gamma_{\pm BX(r)}$ changes appropriately. Thus the apparent ideality of the loading curves at low values of L implies an interesting compensation of the various derivatives of eqns. (12). Their experimental evaluation should be of considerable interest.

3. The adsorption functions in HCl and HClO$_4$ solutions

The adsorption functions of the elements are described below together with a few illustrations of their use for separations. Measurements and discussions emphasize, as mentioned, results for the more concentrated solutions. In those cases in which dilute solutions were studied, agreement with published data was satisfactory (see *e.g.*, refs. 24 and 25).

(*a*) *Alkali metals.* The alkali metals Li through Cs (and presumably Fr) show negligible adsorption in concentrated HCl and HClO$_4$ solutions. In the current context, the minor variations and inversions in adsorbabilities ($D_{Cs} < D_{Li}$) are not of interest. The non-adsorbability of alkali metals at high μ is in agreement with earlier observations on some of these elements[4-6,8].

(*b*) *Alkaline earths (Figs. 6 and 7).* These elements show striking differences in adsorbabilities, particularly in perchlorate solutions.

Beryllium(II) and Mg(II) show little adsorption at high ionic strength.

Calcium is strongly adsorbed from concentrated HClO$_4$ and less, though still significantly, from concentrated HCl. In HCl, the adsorption minimum, $D = ca.$ 2, is located near 6 M; in HClO$_4$ the minimum with $D = ca.$ 7 is near 4.5 M. In HCl, D reaches *ca.* 30 near 12 M; in HClO$_4$, D is *ca.* 10^3 near 11 M, but appears to decrease slightly at higher concentrations.
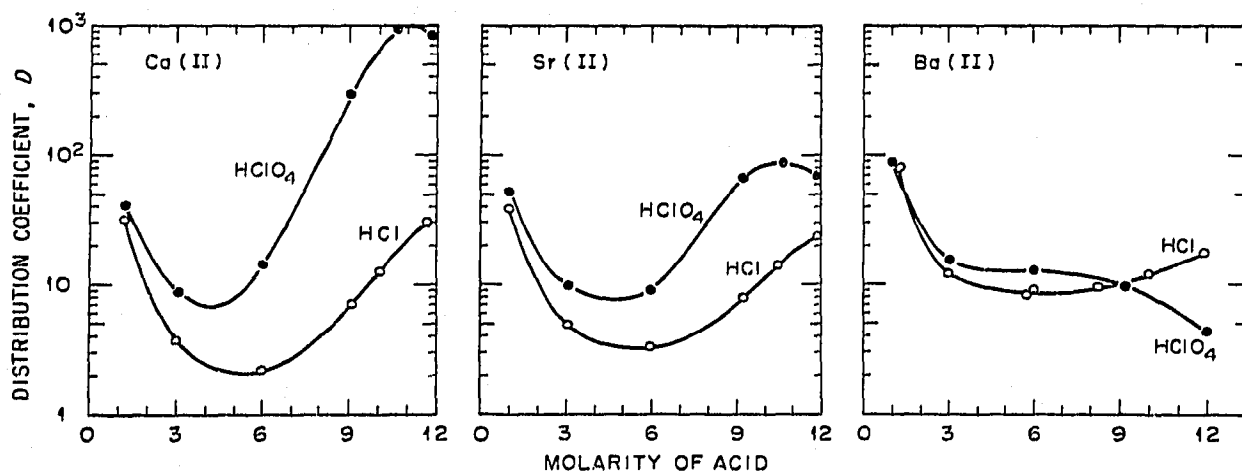
Fig. 6. Adsorption of Ca(II), Sr(II) and Ba(II) from HCl and $HClO_4$ solutions (Dowex 50-X4, 25°).

The behavior of Sr(II) is similar to that of Ca(II), but adsorbabilities at high μ are significantly lower. In HCl the adsorption minimum occurs at $6\,M$ with $D = ca.\ 3$; in $HClO_4$ the minimum occurs near $5\,M$ with $D = ca.\ 8$. In $12\,M$ HCl, D becomes $ca.\ 25$; in $11\,M$ $HClO_4$, $D = 90$. As with Ca(II), there is evidence for a slight decrease in adsorbability above $11\,M$ $HClO_4$.

Adsorbability of Ba(II) at high μ is substantially less than that of Sr(II). In HCl a shallow minimum with $D = 9$ occurs near $6\,M$; D then increases to $ca.\ 18$ in $12\,M$ HCl. In $HClO_4$, D decreases with M $HClO_4$ from $ca.\ 90$ in $1\,M$ to $ca.\ 4$ in $12\,M$; there is no adsorption minimum.

Radium is slightly adsorbed from $9\,M$ HCl and $9\,M$ $HClO_4$ with $D = 5.3$ and 4.2 respectively. There are no adsorption minima.

Our measurements at high μ agree reasonably well with data reported by others. Thus, our results for Mg(II) are in agreement with those of MANN[26] for HCl and $HClO_4$ solutions. The results for HCl with Be(II), Ca(II), Sr(II), Ba(II), and Ra(II) are in reasonable agreement with those of DIAMOND[5] who determined adscrbabilities with a 10–12 % DVB resin. However, the adsorption functions obtained by CHOPPIN AND
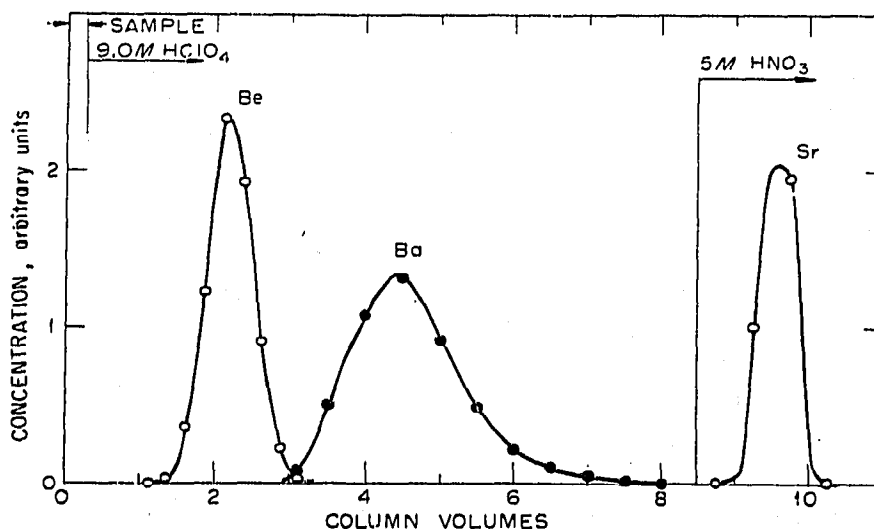
Fig. 7. Separation of Be, Ba and Sr by cation exchange at high ionic strength (Dowex 50-X4, 50°).

Dinius[8] for Ca(II) and Ba(II) in $HClO_4$ differ substantially from ours for M $HClO_4$ > 2. The reason for the disagreement is not known.

The differences in adsorbabilities of the alkaline earths in concentrated perchloric acid are particularly noteworthy and lead to striking separations. Separation of Mg(II) from Ca(II) was recently reported[27]; that of Be(II), Ba(II), and Sr(II) using $HClO_4$ for adsorption and HNO_3 for elution is shown in Fig. 7. While the Be–Ba separation is marginal with the short column used (4 cm), that of Ba(II) from Sr(II) is excellent.

(c) *Scandium(III) and Yttrium(III)* (*Figs. 8 and 11*). Adsorbability of Sc(III) from concentrated $HClO_4$ is larger than that of any other trivalent ion. Adsorbability rises from a minimum $D = 57$ in 3 M to $D > 10^6$ in 9 M $HClO_4$. In HCl adsorbability rises much less dramatically from a minimum $D = 6$ at 5 M to $D = 70$ at 12 M.
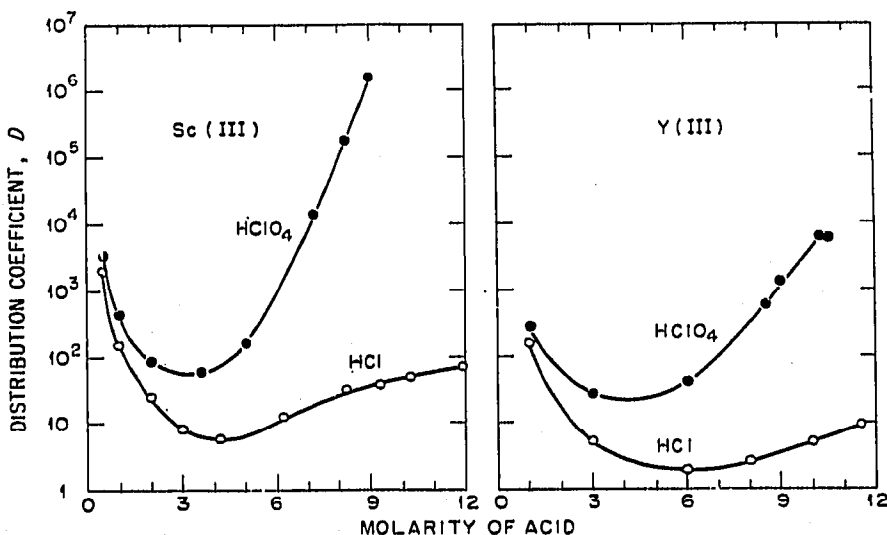
Fig. 8. Adsorption of Sc(III) and Y(III) from HCl and $HClO_4$ solutions (Dowex 50-X4, 25°).

A separation which makes use of the strong adsorption of Sc(III) from 9 M $HClO_4$ (and 9 M HCl) is shown in Fig. 11 and discussed in Section 3e.

The adsorption function of Y(III) is similar to that of Sc(III), but at high ionic strength adsorbability is much less. For Y(III) in 9 M $HClO_4$, D is 10^3; in 9 M HCl, D is only 4. Adsorption minima are at 4 M $HClO_4$ and 6 M HCl with $D = 23$ and 1.9, respectively.

(d) *Rare earths* (*Fig. 9*). The adsorption functions of the lightest and heaviest rare earths, La(III) and Lu(III), apparently define the region of adsorbability of the rare earths. At high μ, as with Sc(III) and Y(III), D is much greater in $HClO_4$ than in HCl. In $HClO_4$ the adsorption functions show minima near 4–5 M and rise steeply thereafter. In HCl the minima are very shallow and occur near 6 M.

For the four rare earths studied, D decreases fairly regularly, for a given medium, with increasing atomic number. Study of other rare earths did not seem warranted since other authors have established that adsorbability of the rare earths in HCl[*,4] and $HClO_4$[8] decreases monotonically with atomic number. Where comparisons can be made, our results are in good agreement with those published.

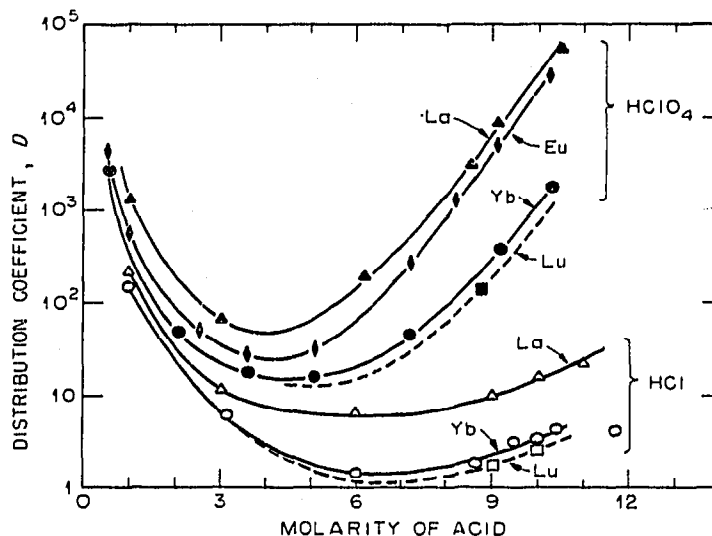* We are indebted to Dr. A. CHETHAM-STRODE for permission to quote these unpublished results.

Fig. 9. Adsorption of rare earths from HCl and HClO$_4$ solutions (Dowex 50-X4, 25°).

(e) *Titanium(IV)* (*Figs. 10 and 11*). Adsorbability of Ti(IV) in HCl first decreases with increasing M to a shallow minimum, $D < 1$, near 6 M and then increases slowly to $D = 10$ in 12 M HCl.

In HClO$_4$ adsorbability of Ti(IV) first decreases to a minimum $D = 6$ near 3 M and then increases markedly with increasing M HClO$_4$ to $D > 10^4$ near 10 M.

A separation involving Ti(IV) in HClO$_4$ is illustrated in Fig. 11. A solution containing the tracers ^{42}K, ^{44}Ti–^{44}Sc in 2.5·10^{-3} M Ti(IV)–12 M HCl was evaporated with 0.5 ml of conc. HClO$_4$ to remove HCl. The solution was adjusted to a final volume of 1 ml with 9 M HClO$_4$ and a small aliquot was added to a 3 cm × 0.2 cm^2 column of Dowex 50-X4 which had been pretreated with 9 M HClO$_4$. On elution with 9 M HClO$_4$, K$^+$ appeared in a sharp band near one column volume (c.v.) while Ti(IV) and Sc(III) (see Section 3c) were retained by the resin. Ti(IV) was removed in a reasonably sharp band with 9 M HCl and Sc(III) with 4 M HCl–0.1 M HF. Although
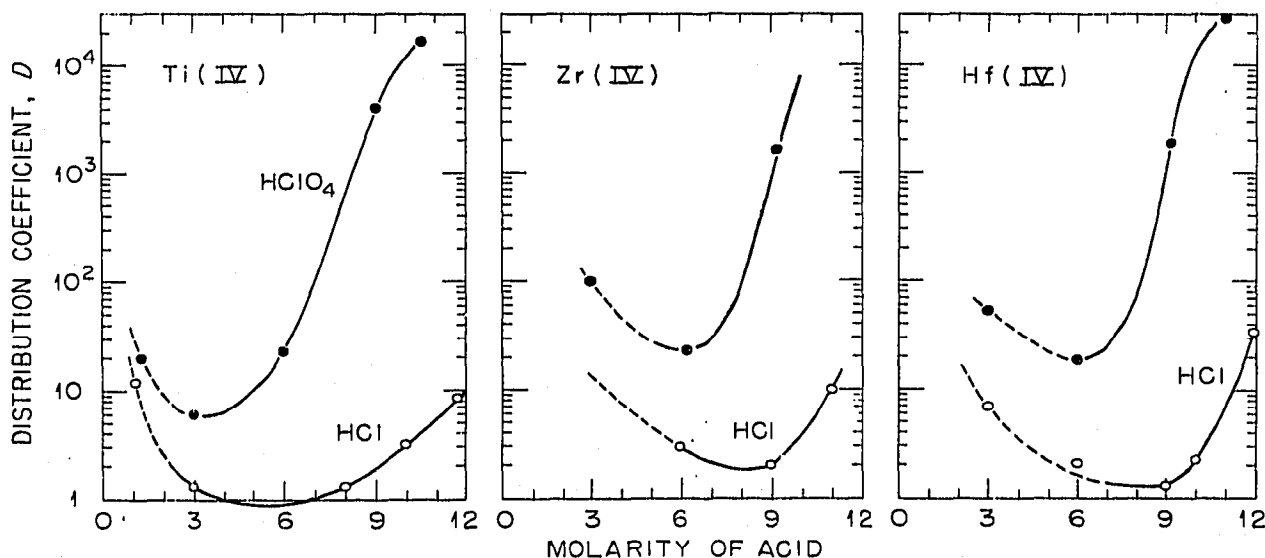
Fig. 10. Adsorption of Ti(IV), Zr(IV), and Hf(IV) from HCl and HClO$_4$ solutions (Dowex 50-X4, 25°).

Sc(III) could also have been eluted with 4 M HCl, an eluent containing HF was selected since it permits more rapid removal of Sc(III) through formation of weakly adsorbed fluoride complexes.

Attempts to carry out similar separations with *ca.* 0.1 M Ti(IV) solutions were unsuccessful; precipitation of Ti(IV) occurred as HCl was removed during the fuming step with concentrated $HClO_4$.
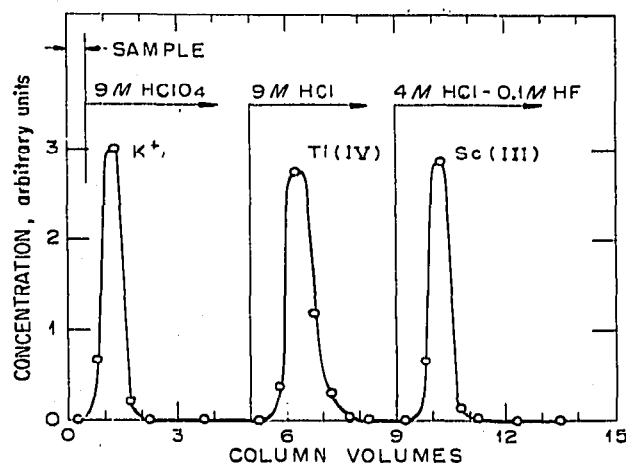

Fig. 11. Separation of K^+, Sc(III) and Ti(IV) by cation exchange at high ionic strength (Dowex 50-X4, 25°).

(f) Zirconium(IV) and hafnium(IV) (*Figs. 10 and 12*). The cation exchange behavior of Zr(IV) and Hf(IV) in dilute or moderately concentrated HCl or $HClO_4$ solutions has been extensively studied (see *e.g.*, ref. 28). Both elements are relatively strongly adsorbed from the dilute acids; while adsorbability falls off rapidly with increasing acidity it is also dependent on metal concentration at a given acidity.

Adsorbability of Zr(IV) and Hf(IV) in HCl reaches a minimum with $D = ca.$ 2 at 6 M; D then rises to *ca.* 40 in 12 M HCl. Our results are in good agreement with those
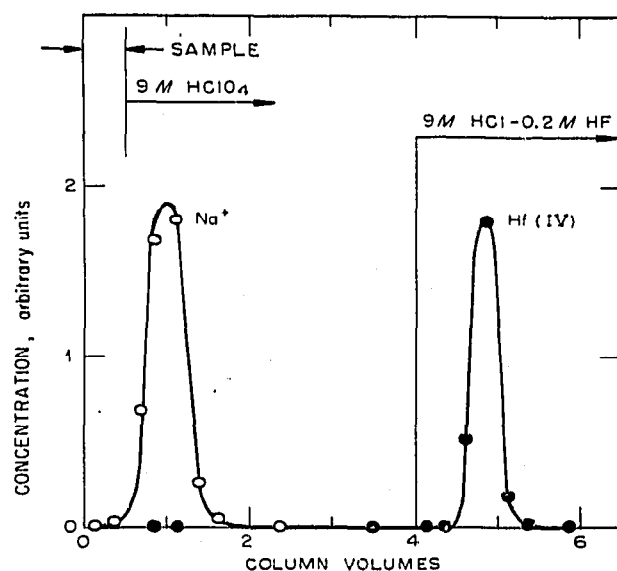
Fig. 12. Separation of Na^+ and Hf(IV) by cation exchange at high ionic strength (Dowex 50-X4, 50°).

of BENEDICT, SCHUMB AND CORYELL[29]. The adsorption function of Hf(IV) is slightly below that of Zr(IV); the differences are sufficient for chromatographic separation of the elements as first demonstrated by STREET AND SEABORG[30].

In $HClO_4$ the adsorbability minimum of Zr(IV) and Hf(IV) is near 6 M with D = ca. 20; D then increases markedly with M $HClO_4$ to ca. $3 \cdot 10^4$ in 11 M. Again, Hf(IV) is slightly less adsorbed than Zr(IV).

A separation involving Hf(IV) in concentrated $HClO_4$ is shown in Fig. 12. It serves to illustrate that Hf(IV) (and presumably also Zr(IV)) in millimolar concentrations may be quantitatively adsorbed from concentrated $HClO_4$ solutions; the usual tendency of these elements to undergo precipitation and other complicating hydrolytic reactions in the absence of complexing agents seems not to interfere at these high acidities.

For the separation of Fig. 12, a 9 M $HClO_4$ solution (0.5 ml) containing $6 \cdot 10^{-3}$ M Hf(IV) with [181]Hf tracer and a typical weakly adsorbed element, [22]Na, was added to a 4 cm $\times$ 0.25 cm^2 column of Dowex 50-X4 which had been pretreated with 9 M $HClO_4$. To improve exchange rates, the column was operated at 50°. On elution with 9 M $HClO_4$, sodium appeared in a sharp band near 1 c.v. while Hf(IV) remained adsorbed. Elution of Hf(IV) was carried out with 9 M HCl–0.2 M HF; this complexing medium conveniently removes Hf(IV) (and Zr(IV)).

(g) *Thorium(IV)* (*Fig. 13*. Traditionally, Th(IV) is the element most difficult to remove from cation exchangers without use of complexing agents. In HCl, D decreases from ca. 10^5 at 0.5 M to ca. 70 at 6 M where its extremely shallow adsorption minimum is located. These results agree reasonably well with data reported by others[4].

The adsorption function in $HClO_4$ is similar to that in HCl at low concentrations. However, because of an extemely rapid increase of D with M $HClO_4$ at high concentration, the distribution coefficient at the adsorption minimum (located at M = ca. 3) is very large, D = ca. 10^3.

The principal cation exchange problem with Th(IV) thus is development of convenient elution methods. Elution in few column volumes requires complexing agents
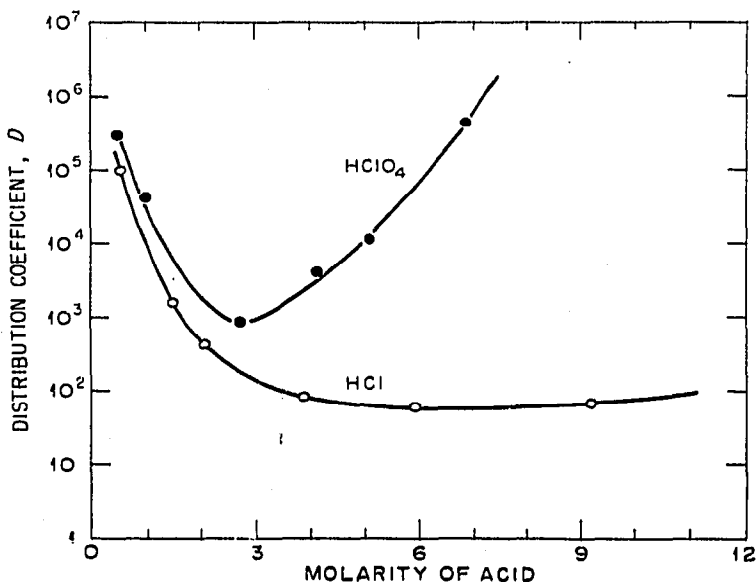

Fig. 13. Adsorption of Th(IV) from HCl and $HClO_4$ solutions (Dowex 50-X4, 25°).

such as oiganic acids, H_2SO_4 and $HClO_4$–HF or HCl–HF mixtures. We shall discuss some of these in later reports.

(*h*) *Vanadium(IV) and (V) (Figs. 14 and 15).* V(IV) is much more strongly adsorbed from concentrated $HClO_4$ than from HCl. Adsorbability in HCl solutions de-
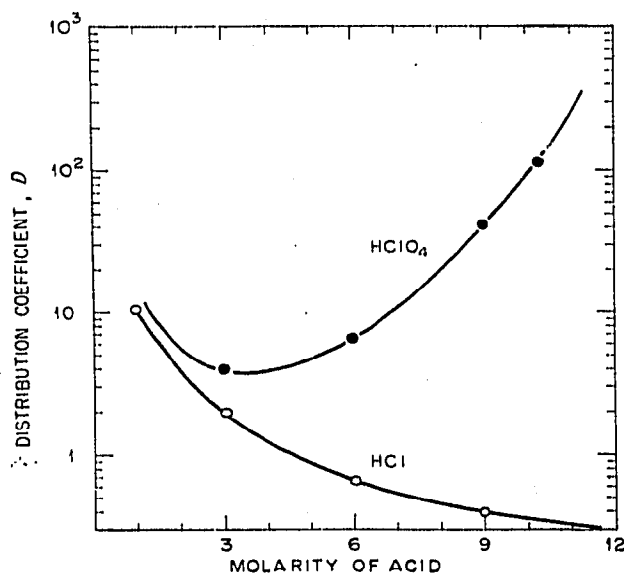

Fig. 14. Adsorption of V(IV) from HCl and $HClO_4$ solutions (Dowex 50-X4, 25°).

creases with increasing M and becomes negligible at high M HCl. In $HClO_4$, after an initial decrease, adsorbability increases rapidly from a minimum $D = 4$ near 3 M to $D = ca.$ 100 near 10 M $HClO_4$.

The strong adsorption of V(IV) from concentrated $HClO_4$ is utilized in the separation shown in Fig. 15. A mixture containing V(IV) and two relatively weakly adsorbed elements, Cr(III) and Ni(II) (see Sections 3*j* and 3*o*) in 9 M $HClO_4$ was added to a small column of Dowex 50-X4. The weakly adsorbed elements were removed in
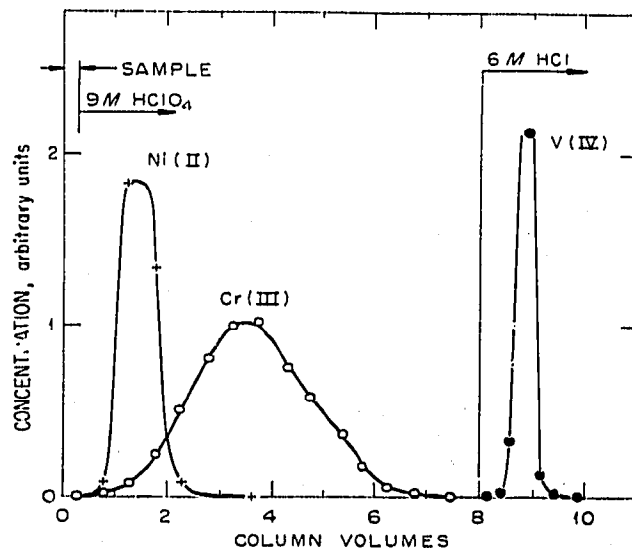

Fig. 15. Separation of Ni(II), Cr(III) and V(IV) by cation exchange at high ionic strength (Dowex 50-X4, 25°).

overlapping bands with 9 c.v. of 9 M HClO$_4$ while V(IV) remained adsorbed; V(IV) was removed in a sharp band with 6 M HCl.

Vanadium(V), like V(IV), is strongly adsorbed from 9 M HClO$_4$ ($D_v > 10^2$) and weakly adsorbed from 9 M HCl, ($D_v = ca.$ 2). In 9 M HClO$_4$, V(V) adsorbs as an intensely colored (brown) band which slowly reduces to a blue V(IV) species. In HCl, V(V) adsorbs as a reddish-brown band, presumably a chloride complex, which rapidly reduces to V(IV).

(i) Niobium(V), tantalum(V) and protactinium(V). Hydrolysis of these elements is particularly troublesome in HClO$_4$ solutions, including concentrated HClO$_4$. Even at tracer concentrations, these elements tend to adsorb irreversibly and irreproducibly on the walls of containers. To estimate D in 9 M HClO$_4$, adsorption measurements were carried out in the presence of small and varying amounts of HF. At 9 M HClO$_4$ and low M HF, the elements are strongly adsorbed and adsorbabilities increase rapidly with decreasing M HF at constant M HClO$_4$. The distribution coefficients at the lowest HF concentration ($3 \cdot 10^{-4}$ M) were all larger than 10^3; these are presumably lower limits for the adsorbabilities in 9 M HClO$_4$.

In 9 M HCl, Nb(V), Ta(V) and Pa(V) are weakly adsorbed. The stock tracer solutions used in the study were prepared by heating appropriate aliquots of [95]Nb, [181]Ta. and [233]Pa in HCl–HF media with excess H$_3$BO$_3$ to volatilize fluoride as BF$_3$. The residual solutions were taken up in excess 9 M HCl and added to small columns of resin which had been pretreated with 9 M HCl–0.1 M H$_3$BO$_3$. In some experiments, particularly with Ta(V), the elution bands tailed suggesting that slowly reversible and adsorbable species tend to form in 9 M HCl media. With 12 M HCl, D_v values of the order of 1–2 were observed for Nb(V), Ta(V) and Pa(V).

(j) Chromium(III) and (VI). Cr(III) is weakly adsorbed ($D_v < 1$) above *ca.* 6 M HCl. In dilute HCl, Cr(III) is strongly adsorbed. However, on heating Cr(III) solutions in HCl, weakly adsorbed species may be formed. Thus in a typical experiment, Cr(III) tracer in 0.5 M HCl was heated several minutes near 95°, cooled to room temperature and added to a small column of Dowex 50-X4 resin. On elution with 0.5 M HCl a small amount of the Cr(III) immediately passed through the column while most of the Cr(III) was strongly adsorbed.

In perchloric acid solutions, the adsorption function of Cr (III) shows a shallow minimum, $D_v = 3.3$ near 6 M and increases slightly with further increase of M HClO$_4$.

Adsorption of Cr(VI) from dilute HCl is negligible ($D_v < 1$). For M HCl $>$ *ca.* 4 adsorbability increases slightly to $D_v = ca.$ 1.6 near 8 M.

In HClO$_4$ adsorption of Cr(VI) is also negligible for $M < ca.$ 4, however, at higher acid concentration, D increases markedly; in 9 M HClO$_4$, D_v is probably considerably larger than 10^2, a surprisingly high value for a negatively charged ion. Since Cr(VI) is reduced by HCl and, presumably by the resin in HClO$_4$; these media cannot be utilized for separations. Estimates of the distribution coefficients were made by adding *ca.* 0.05 M Cr(VI) solutions to the columns and noting, in band elution experiments, the behavior of the unreduced portions.

(k) Molybdenum(VI) (Fig. 16). Adsorbability of Mo(VI) is negligible from 2 M HCl ($D_v < 1$) and increases only slightly with increasing M HCl to $D = 1.6$ at 12 M. Measurements were not attempted with more dilute HCl solutions because of the tendency of this element to form slowly reversible hydrolytic species[31].

In perchloric acid, adsorbability of Mo(VI) is low, $D_v < 1$, in the region 2–4 M

$HClO_4$. Measurements were not carried out below 2 M $HClO_4$ because of expected difficulties from hydrolytic polymerization. Adsorbability of Mo(VI) becomes significant in concentrated $HClO_4$ solutions, increasing from $D = 9$ near 6 M to $D > 10^3$ in 10 M.

(*l*) *Tungsten(VI)* (*Fig. 16*). Adsorbability of W(VI) is low in concentrated HCl; it increases slightly from $D = 1.1$ in 6 M to $D = 2$ in 12 M. Measurements were not carried out below 6 M HCl because difficulties from hydrolytic reactions were expected[31].
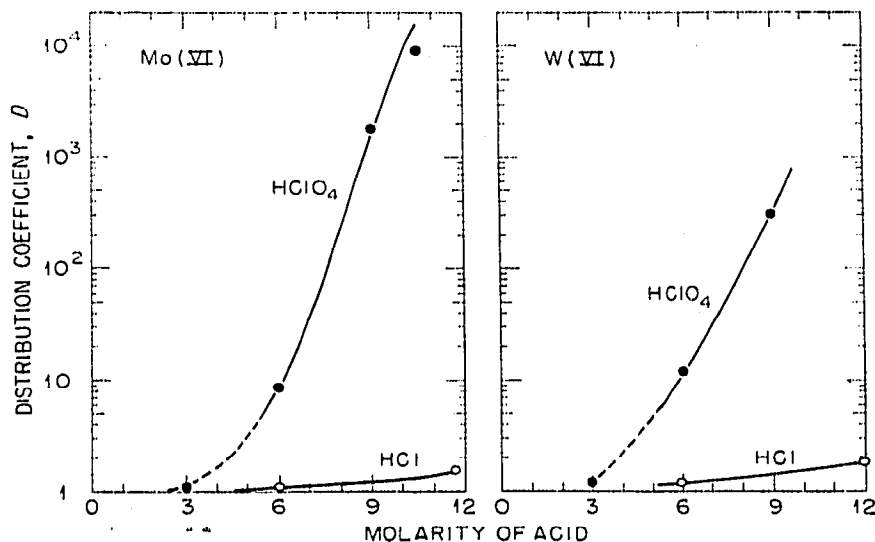
Fig. 16. Adsorption of Mo(VI) and W(VI) from HCl and $HClO_4$ solutions (Dowex 50-X4, 25°).

In perchloric acid adsorbability of W(VI) is low near 3 M and increases rapidly with increasing M to $D > 10^2$ near 9 M.

Adsorption data for perchloric acid concentrations below 6 M $HClO_4$ tended to be erratic (hydrolysis) even at the tracer W(VI) concentrations studied (*ca.* $4 \cdot 10^{-8} M$). Further, although satisfactory column adsorption of W(VI) could be obtained with *ca.* $10^{-7} M$ W(VI) in 9 M $HClO_4$, attempts to carry out separations with *ca.* $10^{-4} M$ W(VI) in 9 M $HClO_4$ were unsuccessful because of precipitation of tungstic acid.

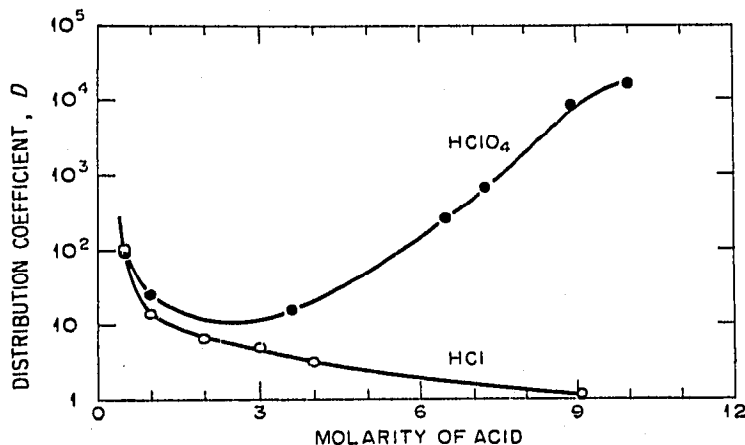(*m*) *Uranium(VI), neptunium(VI) and plutonium(VI)* (*Fig. 17*). U(VI) is strongly

Fig. 17. Adsorption of U(VI) from HCl and $HClO_4$ solutions (Dowex 50-X4, 25°).

adsorbed from dilute HCl and adsorbability decreases with increasing M HCl; above 6 M HCl adsorbability is negligible, $D_v < 1$. Our results for U(VI) are in good agreement with similar data of DIAMOND, STREET AND SEABORG[4]. As might be expected, Np(VI) and Pu(VI) adsorb very similarly[1]. In the present study, low adsorbability ($D_v < 1$) was confirmed for Np(VI) and Pu(VI) in 9 M HCl solutions.

In HClO$_4$, adsorbability of U(VI) decreases from $D = 100$ near 0.5 M to a minimum $D = 10$ near 2.5 M, then increases to $D > 10^4$ in 10 M HClO$_4$. In 9 M HClO$_4$, (containing small amounts of Cl$_2$ gas) Np(VI) and Pu(VI) were found to be strongly adsorbed, $D > 100$. However, complete adsorption functions for Np(VI) and Pu(VI) in HClO$_4$ were not determined since they are probably very similar to that of U(VI).

In other oxidation states U, Np and Pu are only slightly adsorbed from HCl at high μ according to published data[4] for U(IV), Np(IV), Np(V), Pu(III) and Pu(IV). However, in conc. HClO$_4$ strong adsorption will probably occur for all oxidation states, including, presumably, the $+$ 5 state.

(n) *Transplutonium elements*. The adsorption behavior of the trivalent transplutonium elements in HCl has been extensively studied by others[4,7]. At low M HCl their adsorption is similar to that of the rare earths, but at high M HCl the trivalent transplutonium elements are less strongly adsorbed than the rare earths and a group separation becomes possible. We have included Am(III) and Cm(III) in our studies and found, in agreement with the earlier work with similar Dowex 50 resins that $D_v < 1$ for both elements at M HCl > *ca.* 6.

In HClO$_4$, the adsorption function of Am(III) parallels that in HCl at low acidity; however, near 4 M HClO$_4$ adsorbability increases rapidly from a minimum $D = ca.$ 10 to $D > 10^4$ near 10 M HClO$_4$. Our results for Am(III) are in excellent agreement with similar data of CHOPPIN AND DINIUS[8]. Strong adsorption was also found for Cm(III) in 9 M HClO$_4$; presumably all of the trivalent trans-plutonium elements are strongly adsorbed by Dowex 50 from concentrated HClO$_4$.

Concentrated HClO$_4$ solutions thus appear to be unique media from which all actinides (and indeed most α-emitters) from Ac(III) through the transplutonium elements may be adsorbed.

(o) *Manganese(II), cobalt(II), copper(II) and nickel(II)*. (*Figs. 18 and 19*). The divalent transition elements, Mn(II), Co(II), Ni(II) and Cu(II) have very similar adsorption functions in HCl. They are adsorbed from dilute HCl; but above 6 M HCl, D becomes less than unity. In HClO$_4$ adsorbability of Co(II), Cu(II) and Ni(II) is only slightly greater than from HCl solutions of the same concentration. However, Mn(II) is markedly more strongly adsorbed from concentrated HClO$_4$ solutions than from the corresponding HCl solutions. Adsorbability of Mn(II) increases from a minimum, $D = 5.5$ near 5 M HClO$_4$ to $D = ca.$ 700 in 12 M HClO$_4$.

The strong adsorption of Mn(II) from concentrated HClO$_4$ leads to interesting separations. A typical experiment is shown in Fig. 19 which illustrates the separation of Mn(II) from a relatively weakly adsorbed element, Co(II). A small aliquot of solution containing ^{54}Mn and ^{60}Co tracers in 9 M HClO$_4$ was added to a 0.25 cm^2 × 3 cm column of Dowex 50-X4 pretreated with 9 M HClO$_4$. On elution with the same eluent, Co(II) appeared in the effluent in peak concentration near 1.7 c.v. while Mn(II) remained adsorbed. It was eluted in a sharp band with 9 M HCl.

(p) *Iron(III)* (*Fig. 20*). Adsorbability of Fe(III) from HCl solutions first decreases with increasing acid concentration to a minimum $D \approx 1$ near 4 M, then increases
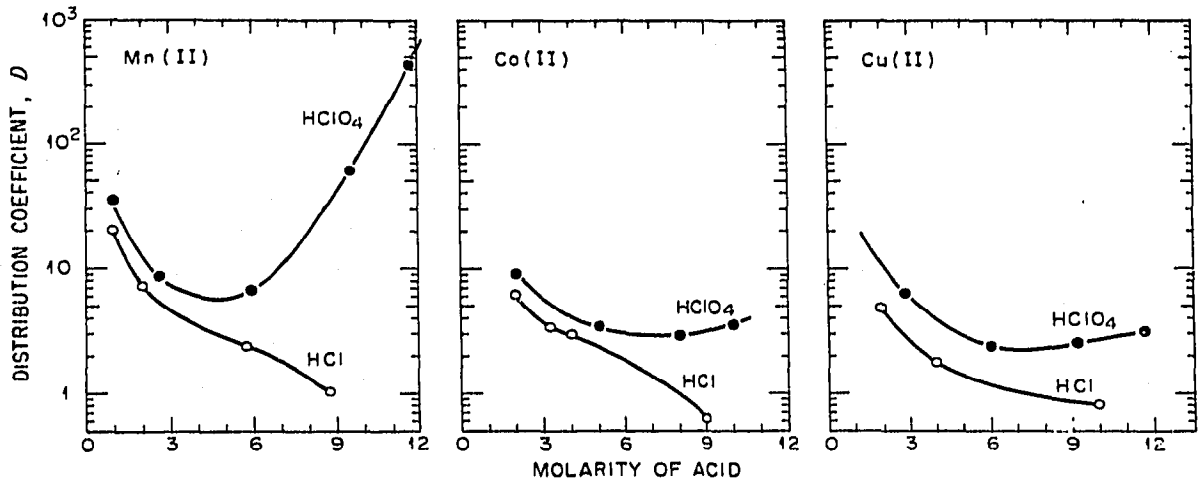
Fig. 18. Adsorption of Mn(II), Co(II) and Cu(II) from HCl and HClO$_4$ solutions (Dowex 50-X$_4$, 25°).
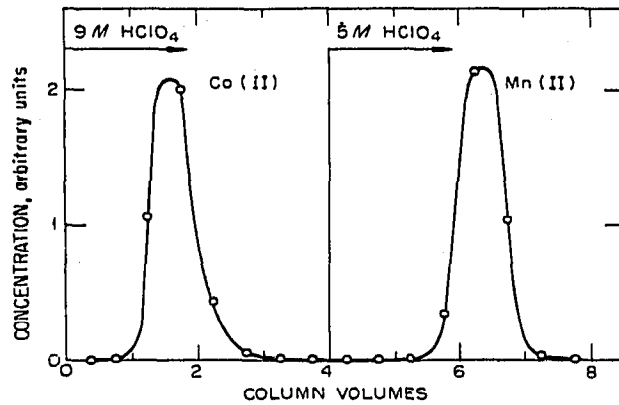
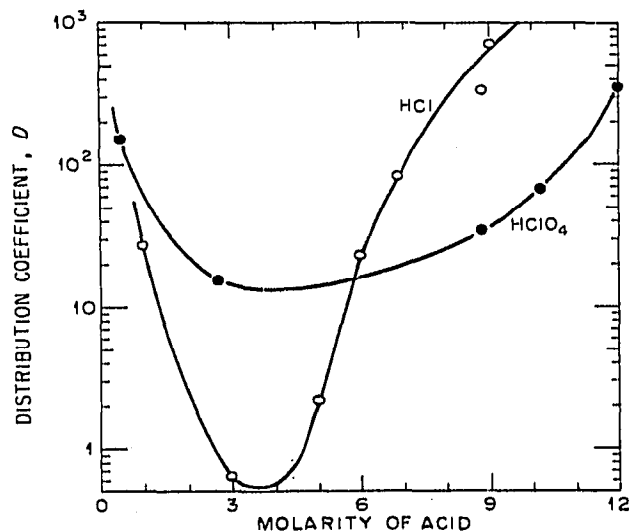Fig. 19. Separation of Co(II) and Mn(II) by cation exchange at high ionic strength (Dowex 50-X$_4$, 50°).

Fig. 20. Adsorption of Fe(III) from HCl and HClO$_4$ solutions (Dowex 50-X$_4$, 25°).

rapidly to $D = ca.$ 10^3 near 10 M. The present results with the 4 % crosslinked resin essentially confirm earlier measurements[6] with a more highly crosslinked (12 %) Dowex 50 resin. However, at low M HCl adsorbability of Fe(III) is lower with the 4 % resin while, in concentrated HCl, it is almost a factor of ten higher than with the 12 % resin. This unusual influence of cross linking on adsorbability at high HCl concentrations was also observed and discussed by TITZE AND SAMUELSON[32].

In $HClO_4$, the adsorption function of Fe(III) shows a shallow minimum near 4 M with $D = ca.$ 10; D increases slowly to $ca.$ 350 in 12 M $HClO_4$.

(*q*) *Technetium(VII) and rhenium(VII)*. Adsorbability of Tc(VII) and Re(VII) is negligible from HCl solutions. In $HClO_4$, adsorbability is also small though slight adsorption with $D_v \approx 1$ occurs in relatively concentrated $HClO_4$ solutions (9 M). In these measurements, small amounts of chlorine gas were added to prevent reduction. In some experiments with Tc tracer (^{99}Tc) in which chlorine was not used, ^{99}Tc was strongly adsorbed from concentrated $HClO_4$ presumably in the form of a lower oxidation state.

(*r*) *Platinum elements*. It is rather well established that the chloride complexes of the platinum elements are not adsorbed from HCl by cation exchangers. For the present study, a series of confirmatory measurements was carried out with Ru(IV), Rh(III), Pd(II), Pd(IV), Os(IV), Ir(IV) and Pt(IV). Negligible adsorption was found for these ions in the range 0.2–9 M HCl.

Adsorbability measurements were not carried out in $HClO_4$ solutions because of uncertainties regarding species and oxidation states of these elements in these media. Significant adsorption of Pd, Rh and Ir in dilute $HClO_4$ has been reported[33]; presumably, the elements were in their higher oxidation states.

(*s*) *Silver(I) and gold(III)*. Adsorbability of Ag(I) was negligible, $D_v < 1$, from 0.2–9 M HCl. In $HClO_4$, adsorbability decreases from $D = 11$ in 1 M $HClO_4$ to a shallow minimum, $D = 3$, near 7 M $HClO_4$; it then increases to $D = 9$ in 10 M $HClO_4$.

Au(III) is strongly adsorbed from moderately concentrated and concentrated HCl. The adsorption function found here is similar to that reported earlier[6] for a resin of higher crosslinking (12 % DVB). However, the values of D with the present 4 % resin are considerably larger than for the 12 % resin[6]. A similar inverse crosslinking effect was observed with Fe(III) (see Section 3 p).

Adsorption of Au(III) was not studied in $HClO_4$ media since reduction and precipitation occurs in the absence of stabilizing complexing agents.

(*t*) *Zinc(II), cadmium(II) and mercury(II)* (*Fig. 21*). In HCl adsorbabilities of Zn(II), Cd(II) and Hg(II) decrease rapidly with increasing M HCl and become negligible above $ca.$ 2, 1 and 0.1 M HCl, respectively.

In dilute $HClO_4$, Zn(II), Cd(II) and Hg(II) are all significantly adsorbed. Adsorbabilities of Zn(II) and Cd(II) decrease to minima near 6 and 4 M $HClO_4$, respectively; D then increases with M $HClO_4$. Adsorption of Hg(II) only decreases with increasing M $HClO_4$.

(*u*) *Aluminum(III), gallium(III), indium(III) and thallium(III)* (*Fig. 22*). Adsorbability of Al(III) decreases with increasing M HCl to $D = ca.$ 4 near 3 M and $D = ca.$ 1 at 12 M HCl. In $HClO_4$, the adsorption function has a shallow minimum near 6 M where $D = ca.$ 5; in 12 M $HClO_4$, $D = ca.$ 20.

Adsorption of Ga(III) in HCl increases rapidly from its minimum $D = 1.5$ near 4 M to $D = ca.$ 800 near 10 M; D decreases slightly with further increase of M HCl.
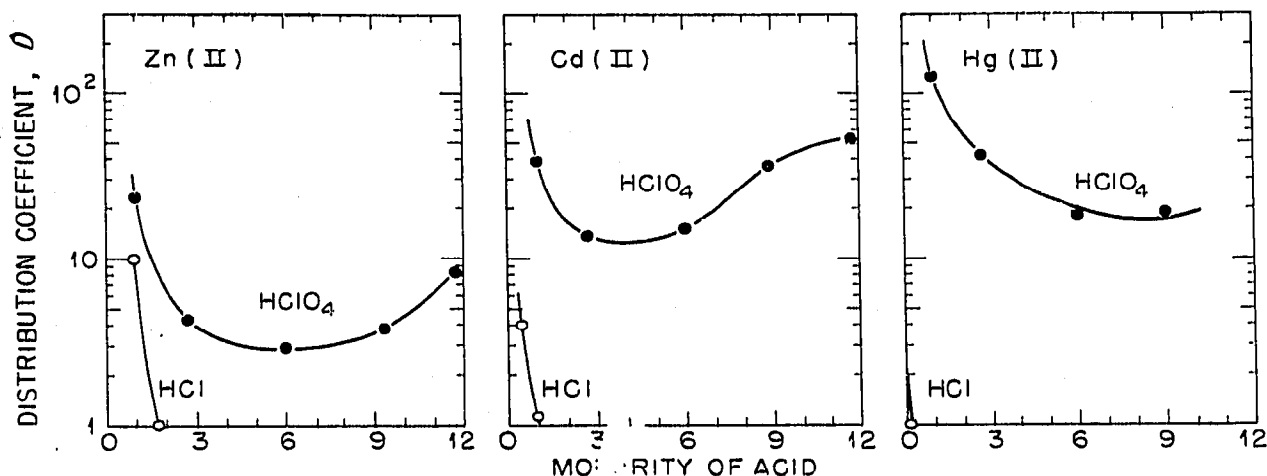
Fig. 21. Adsorption of Zn(II), Cd(II) and Hg(II) from HCl and HClO$_4$ solutions (Dowex 50-X4, 25°).

In HClO$_4$, adsorption is minimum near 4 M and increases rapidly to $D = ca.$ 10^3 at 12 M.

Adsorbability of In(III) decreases rapidly with increasing M HCl and becomes negligible above $ca.$ 1 M HCl. In HClO$_4$, an adsorption minimum occurs near 5 M where $D = ca.$ 10. In 12 M HClO$_4$, D is larger than 10^2.

Tl(III) is weakly adsorbed near 1 M HCl; adsorption increases to a shallow maximum $D = ca.$ 10 near 9 M. The adsorption function in HCl is reminiscent of that for Au(III) but is an order of magnitude lower. In HClO$_4$, adsorbability decreases rapidly with M; there appears to be a shallow minimum near 5 M. The results at higher acid concentrations are in doubt because of the possibility of reduction (by the resin) of Tl(III) to Tl(I).

The results for In(III), Ga(III) and Tl(III) in concentrated HCl solutions are consistent with the earlier data[6] obtained with a 12 % crosslinked resin except that, as with Fe(III) and Au(III), adsorbabilities with the 4 % resin are larger at high μ.

(v) *Germanium(IV) and tin(IV)*. Adsorbability of Ge(IV) and Sn(IV) is negligible from 9 M HCl. These elements have been reported[24] to be adsorbable from dilute HCl but adsorbability falls off rapidly since apparently non-adsorbable chloride complexes are formed.

Adsorbability of Ge(IV) and Sn(IV) in HClO$_4$ was not studied because of the tendency of these elements to hydrolyze and precipitate in these media.
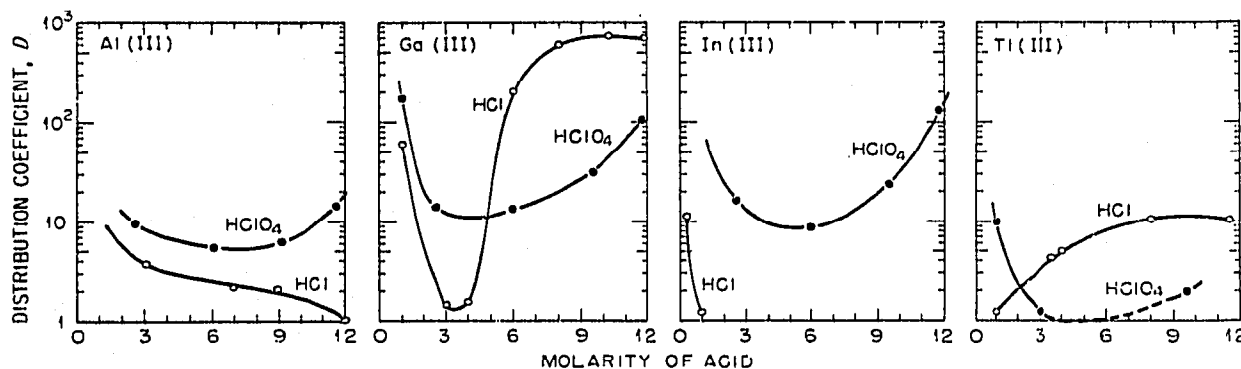

Fig. 22. Adsorption of Al(III), Ga(III), In(III) and Tl(III) from HCl and HClO$_4$ solutions (Dowex 50-X4, 25°).

(*w*) *Lead(II)* (*Fig. 23*). In HCl, adsorbability of Pb(II) decreases rapidly with increasing acid concentration to $D < 1$ above 1.5 M HCl.

In $HClO_4$, adsorbability of Pb(II) decreases less rapidly with acid concentration to a minimum $D = 13$ near 4 M, then slowly increases to $D = ca.$ 60 near 10 M.
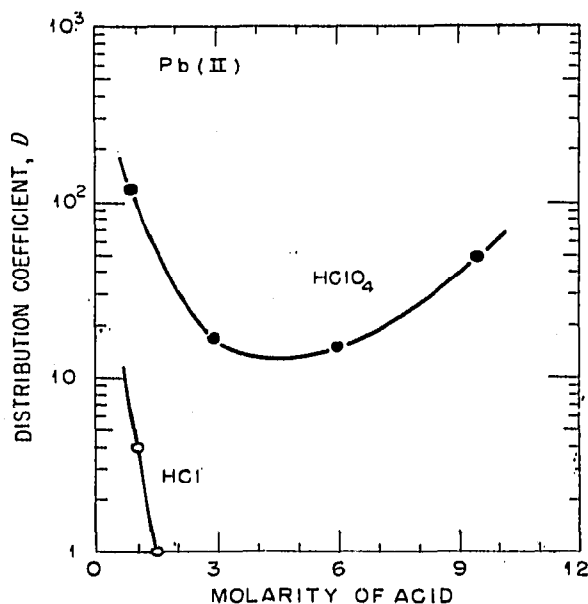

Fig. 23. Adsorption of Pb(II) from HCl and $HClO_4$ solutions (Dowex 50-X4, 25°).

(*x*) *Antimony(III) and (V) and bismuth(III)* (*Figs. 24 and 25*). Sb(III) and Bi(III) are adsorbable from dilute HCl but adsorbability decreases rapidly with increasing M HCl. For Sb(III), $D < 1$ above 3 M HCl while for Bi(III), $D < 1$ above *ca.* 0.5 M HCl.

In $HClO_4$, adsorbability of Sb(III) increases from a shallow minimum, $D = 1.5$ near 6 M to $D = ca.$ 50 near 11 M. Bi(III) is strongly adsorbed at all $HClO_4$ concentrations; its adsorption minimum lies near 4 M where $D = 40$.

In HCl, Sb(V) is strongly adsorbed in the range 9–12 M where $D_v = ca.$ 2,000. These values are markedly higher than the value reported earlier with a 12 % Dowex 1
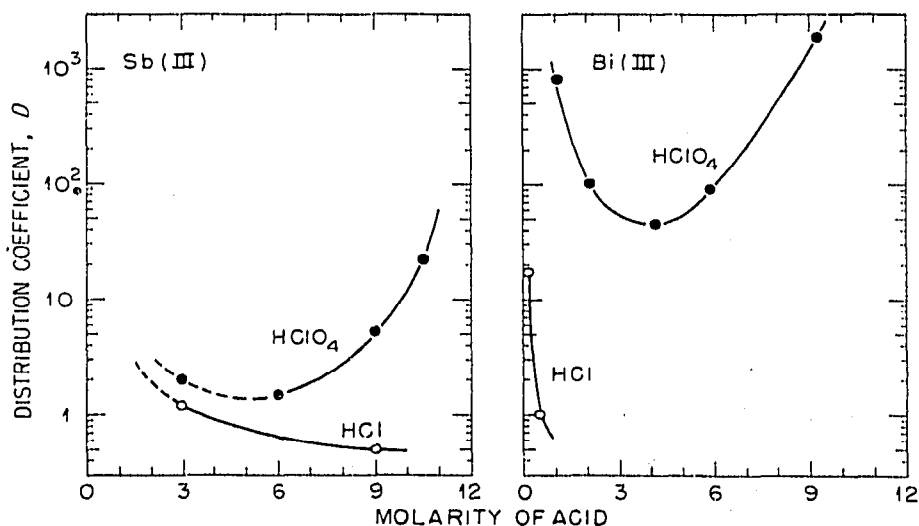

Fig. 24. Adsorption of Sb(III) and Bi(III) from HCl and $HClO_4$ solutions (Dowex 50-X4, 25°).

resin. The error in earlier measurements (by the batch distribution method) may have resulted from presence of the weakly adsorbable (tracer) Sb(III).

Adsorbability measurements of Sb(V) tend to be erratic for M HCl < 9. When Sb(V) was adsorbed from concentrated HCl, slow leak-through occurred on elution with 6–8 M HCl–Cl_2 solutions, although most of the Sb(V) remained strongly adsorbed. Presumably this partial elution results from relatively slow hydrolytic reactions of Sb(V) (see e.g., ref. 34).

The HCl concentration at which Sb(V) adsorption is carried out also affects the rate of reduction of Sb(V) to Sb(III) with iodide. This reduction is useful for elution of antimony as illustrated in Fig. 25 with a separation of Sb from Te. If adsorption is
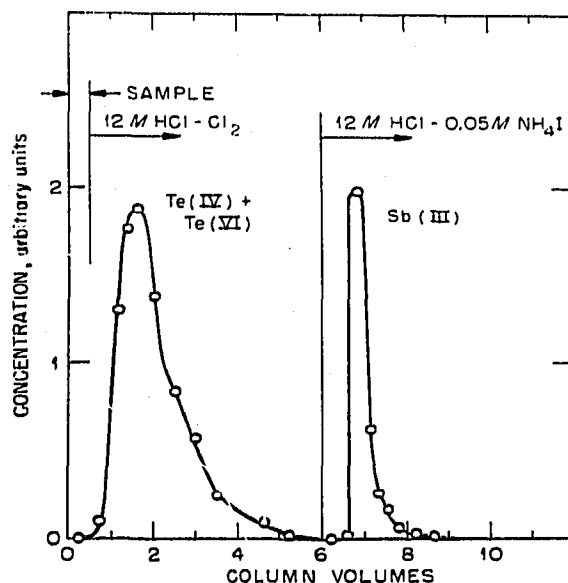

Fig. 25. Separation of Te(IV) and Te(VI) from Sb(V); elution of Sb(V) by reduction to Sb(III) (Dowex 50-X4, 25°).
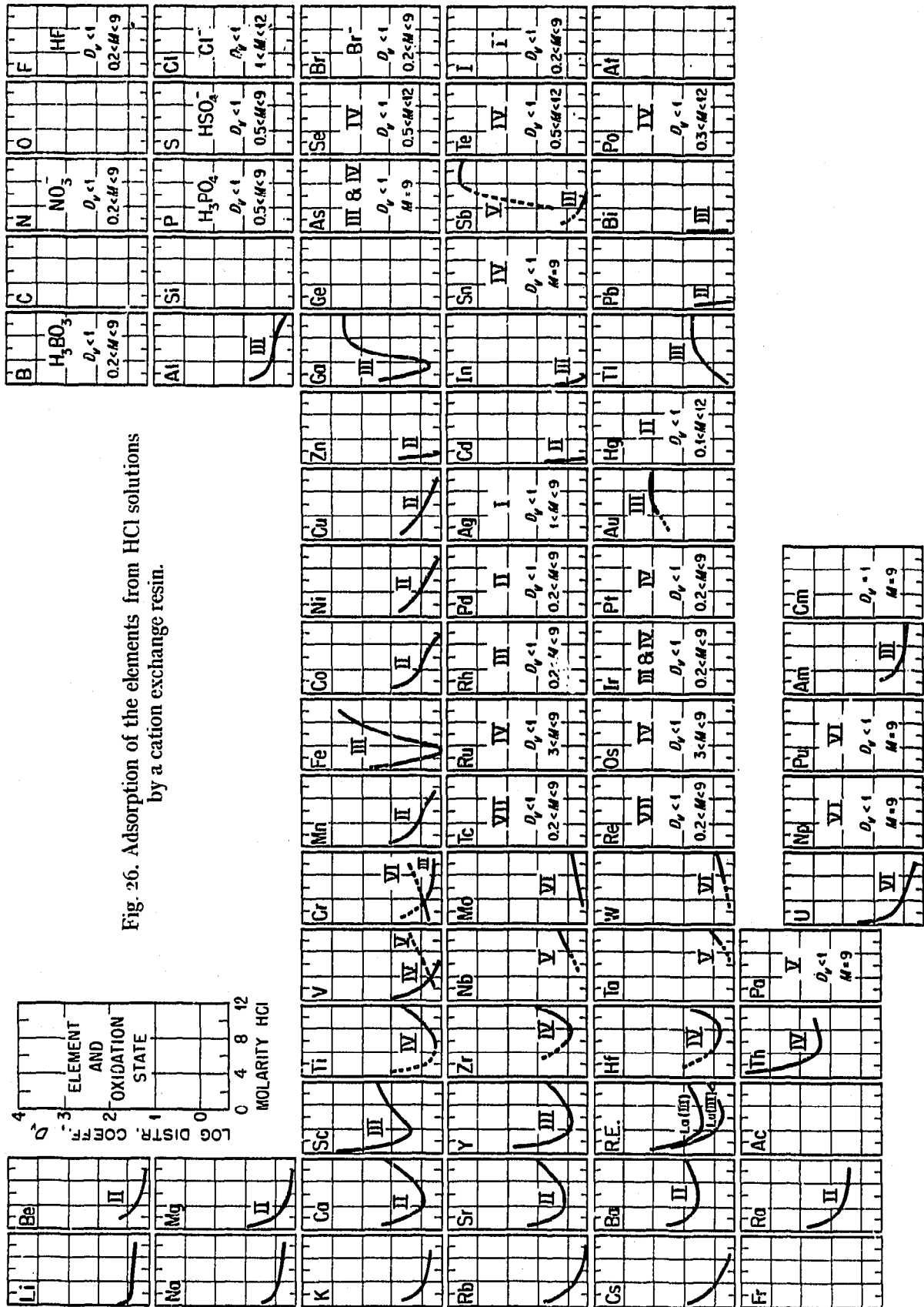
carried out from 10–12 M HCl and reduction with 10–12 M HCl containing ca. 0.05 M NH_4I, immediate and quantitative elution of Sb (as Sb(III)) occurs. However, if adsorption is carried out at M HCl ≤ 8 and elution with the same 10–12 M HCl–0.05 M NH_4I, incomplete removal and severe tailing occur.
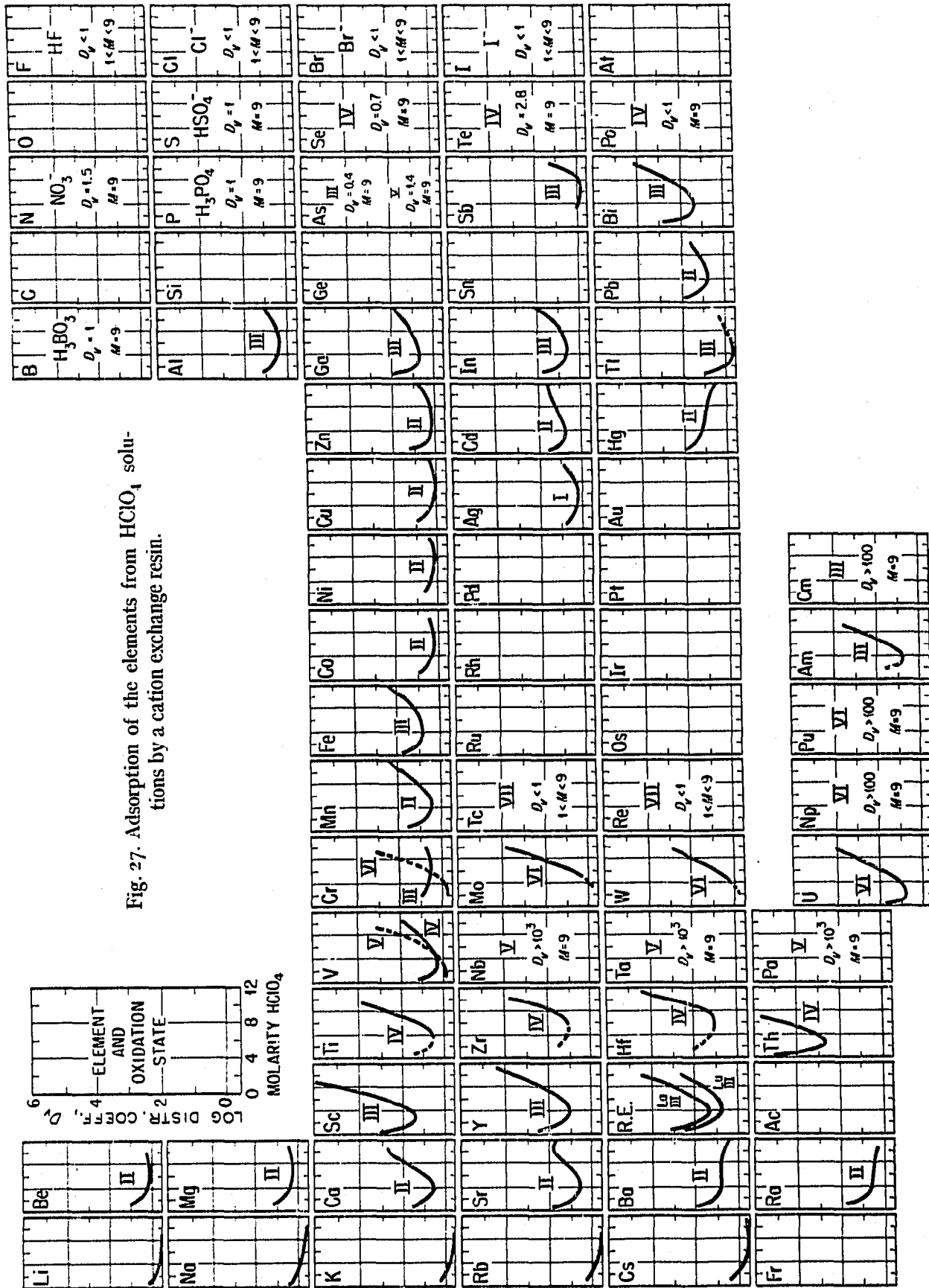
(y) Arsenic(III) and (V), selenium(IV), tellurium(IV) and polonium(IV). These elements are negligibly adsorbed from 9 M HCl and 9 M $HClO_4$ solutions. A cursory examination showed that adsorbabilities are also low (D_v < 1.5) from more dilute solutions (0.2–1 M HCl or $HClO_4$).

(z) Other non-metals. Adsorbability measurements were carried out with HCl and $HClO_4$ solutions containing a number of non-metallic elements as their common acids: H_3BO_3, HNO_3, HF, HCl, HBr, HI, H_2SO_4 and H_3PO_4. Negligible or only slight adsorbability was observed for these acids over a relatively wide range of HCl and $HClO_4$ concentrations (ca. 0.2 or 1 M to 9 M).

CONCLUSIONS

The cation exchange data for the elements in HCl and $HClO_4$ solutions are summarized in Figs. 26 and 27 as plots of log D_v versus molarity of acid. These adsorption

Fig. 26. Adsorption of the elements from HCl solutions by a cation exchange resin.

Fig. 27. Adsorption of the elements from $HClO_4$ solutions by a cation exchange resin.

ELEMENT AND OXIDATION STATE

LOG DISTR. COEFF., D_v

MOLARITY $HClO_4$

functions are comparable; they refer to the same resin (Dowex 50-X4) and most of them were obtained at "tracer" loading ($L < 0.01$). Only for Bi(III), Ti(IV), Hf(IV), Zr(IV) and Mo(VI) in $HClO_4$ was it necessary to operate at higher concentrations; but even for these, loading was less than 10 % at the highest adsorbabilities measured. While adsorbabilities in HCl and $HClO_4$ often differ widely, the adsorption functions have a number of common features. Thus, at low ionic strength, most elements show a decrease of D with μ, as expected. However, several elements (e.g., Zn(II), Cd(II), Hg(II), Pb(II), In(III) and Bi(III)) show a precipitous decrease in adsorbability in dilute HCl; for these there is no resurgence of adsorbabilities at high μ. These elements are strongly complexed by chloride ions and their complexes (as those of many other elements such as the platinum elements) are non-adsorbable. Conclusions regarding the charge of these complexes cannot be drawn from the ion exchange data alone since at least some negatively charged complexes can be adsorbed by cation exchangers[6].

Many elements show adsorption minima in HCl and $HClO_4$ solutions. In HCl the minima are usually shallower than in $HClO_4$ and the distribution coefficients at the minima are lower. This is a reflection of the slower increase of D with M in HCl compared with $HClO_4$. For some elements this slow increase of D in HCl, or the lack of such increase, results from formation of non-adsorbable chloride complexes at high μ. For others, e.g., Ca(II) and Sr(II), the difference in adsorbabilities in HCl and $HClO_4$ solutions presumably is not due to formation of chloride complexes. Thus comparison of distribution coefficients in HCl and $HClO_4$ is often not sufficient to decide if complexing reactions occur. However, measurement of distribution coefficients in HCl and $HClO_4$ mixtures at constant μ often permits identification of complexing reactions and evaluation of the stability quotients.

The excellent adsorption which occurs at high ionic strength and the differences in adsorption functions between HCl and $HClO_4$ solutions may be utilized for the separations of the elements, both individually and in groups. For example, a number of elements can be adsorbed from concentrated $HClO_4$ solutions and thus be separated from the weakly adsorbed elements. The adsorbed elements may then be eluted, often sequentially, with concentrated HCl or more dilute HCl and $HClO_4$, or HCl–$HClO_4$ mixtures. However, for many purposes such group separations can be carried out more efficiently with HCl–$HClO_4$ mixtures containing small amounts of HF; our studies with such mixed acid systems will be discussed in subsequent publications.

SUMMARY

A broad survey of the cation exchange behavior of the elements in HCl and $HClO_4$ solutions is presented and adsorption functions are given. The results are also summarized in the form of two "Periodic Tables" which give the distribution coefficients of the elements as a function of M HCl and M $HClO_4$.

Many elements are strongly adsorbed from concentrated $HClO_4$ solutions. There

are large differences in adsorbability between HCl and $HClO_4$ solutions, particularly at high ionic strength. Application of these data to high ionic strength cation exchange separations is illustrated.

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