ION-EXCHANGE PROCEDURES

IX. CATION EXCHANGE IN HBr SOLUTIONS[*,**]

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In a previous study[2], the adsorption behavior of the elements on a Dowex 50 cation exchange resin in HCl and $HClO_4$ solutions was measured over a wide range of acid concentrations. Many elements showed adsorption minima in these acids followed by a rise in adsorbability at high acid concentrations. Marked differences in adsorbabilities of the elements at high acid concentrations were shown to permit excellent separations.

In the present paper, cation exchange adsorbabilities of the elements in dilute to concentrated (12 M) HBr solutions are described. As in HCl and $HClO_4$ solutions, many elements show adsorption minima in HBr solutions. Adsorption data for relatively concentrated HBr solutions are compared with similar data for HCl and $HClO_4$ solutions. A number of typical column separations employing relatively concentrated HBr solutions as eluents are described.

EXPERIMENTAL

Adsorbabilities of the elements were determined by the same batch equilibration or column methods described earlier[2] and with the same batch of Dowex 50-X4 resin (270–325 mesh, in water). The resin had a capacity of 5.12 equivalents per kg dry resin. The radiometric and other methods of analysis were described earlier[2].

Adsorbabilities were expressed as volume distribution coefficients, D_v (amount adsorbed per liter resin bed/amount per liter solution). Weight distribution coefficients, D (amount adsorbed per kg dry resin/amount per liter solution) were converted to D_v values by the relationship $D = D_v/\rho$. The value of $1/\rho$ (liters of bed per kg dry resin) for the resin in water is 3.40. In 1, 3, 6, 9 and 12 M HBr, $1/\rho$ is 3.02, 2.63, 2.32, 2.13 and 2.02, respectively.

All distribution coefficients, except when otherwise specified, refer to conditions of low loading (< 1 % capacity) of the resin by the elements in question.

The columns were prepared from polypropylene tubing, usually *ca.* 0.6 cm in diameter. The tubing was heated and pulled to a tip at one end, and a porous Teflon plug inserted to retain the resin. Resin beds 2 to 6 cm long were usually used in determining distribution coefficients or for separations. The columns were placed in a water jacket through which water of controlled temperature (usually 25°) was

pumped. To improve elution kinetics, some separations were carried out at elevated temperatures and with columns prepared from a fine fraction of the resin (20–30 μ diameter, in water).

HBr solutions were usually prepared by dilution of 48 % (ca. 9 M) reagent grade HBr. Stock solutions more concentrated than 9 M HBr were prepared by saturating 48 % HBr solution with gaseous HBr.

Stock solutions of the elements (usually radioactive tracers[2]) were prepared by evaporating solutions of the elements in HCl or HNO_3 with excess 9 M HBr to volatilize the HCl or decompose HNO_3. The residues were taken up with the appropriate HBr solution. In some cases, stock solutions were prepared by dissolving bromide salts or oxides of the elements in appropriate HBr solutions.

Special precautions were taken in preparing stock solutions of the platinum elements since their halide complexes, though very stable, are sometimes formed slowly[3]. Stock solutions of Pt(IV) and Pd(II) were prepared by evaporating HCl stock solutions containing $PtCl_6^{2-}$ and $PdCl_4^{2-}$ with excess 9 M HBr; conversion of Pt(IV) and Pd(II) chloride complexes to the corresponding bromide complexes has been reported to be rapid under these conditions[4]. Stock solutions of Rh(III) and Ir(IV) were prepared by evaporating small aliquots of HCl solutions of Rh(III) and Ir(IV) with about 1 ml of concentrated $HClO_4$ to a volume of ca. 0.1 ml. Excess 9 M HBr was added, and the solutions were heated near the boiling point for several hours. Liquid bromine was added to assure that Ir(IV) would be formed. A stock solution of Ir(III) was prepared by shaking a solution of Ir(IV) in 9 M HBr with silver metal; reduction of Ir(IV) to Ir(III) occurs rapidly. A stock solution of Ru(IV) was prepared by prolonged refluxing of small aliquots of Ru(IV) in HNO_3 with excess 9 M HBr. Os(IV) stock solutions were prepared by dissolving OsO_4 in 9 M HBr. Although reduction of the volatile tetroxide to Os(IV) species is slow in dilute HBr, reduction is rapid in hot, 9 M HBr solutions[5]. The Os(IV) stock solution was heated near the boiling point for several hours to assure formation of the higher bromide complexes of Os(IV).

Stock solutions of Au(III) were prepared by adding an excess of the appropriate HBr solution to small aliquots of Au(III) in HCl. Conversion of the chloroaurate complex to the bromoaurate complex is rapid in the presence of excess HBr[6].

Special precautions were also taken in preparing stock solutions and working with solutions of elements which are volatile in HBr, e.g., Ge(IV), Se(IV), As(III). Small aliquots of tracer solutions of these elements in ca. 0.1 M NaOH were added (at room temperature) to an excess of the appropriate HBr solution. Since Ge(IV) is especially volatile at high M HBr, Ge(IV) solutions were kept in stoppered containers as much as possible and sampled carefully to minimize losses. Solutions of volatile halogen acids, e.g., HCl, HF, were prepared at room temperature by dilution of the acids with excess HBr solution.

RESULTS AND DISCUSSION

1. Adsorption functions in HBr solutions

In this section, the adsorption functions of the elements are described and use of these functions for column separations is illustrated. Since little has been published on the cation exchange behavior of elements in concentrated HBr solutions, the con-

centrated region is particularly emphasized. Our data at low HBr concentrations, in so far as comparisons can be made, are in satisfactory agreement with the measurements of FRITZ AND GARRALDA[7] for thirty-six elements in o.5 M HBr solutions.

(a) *Alkali metals* (*Figs. 1 and 2*). Adsorbabilities of the alkali metals, K^+ to Fr^+, gradually decrease with increasing M HBr; for Li^+ and Na^+, adsorbabilities first decrease to minima and then increase in the region 4 to 12 M HBr (Fig. 1). At high M HBr inversion of the elution order occurs, *i.e.*, Li^+ is more strongly adsorbed than Na^+, and Na^+ is more strongly adsorbed than the higher alkali metals.
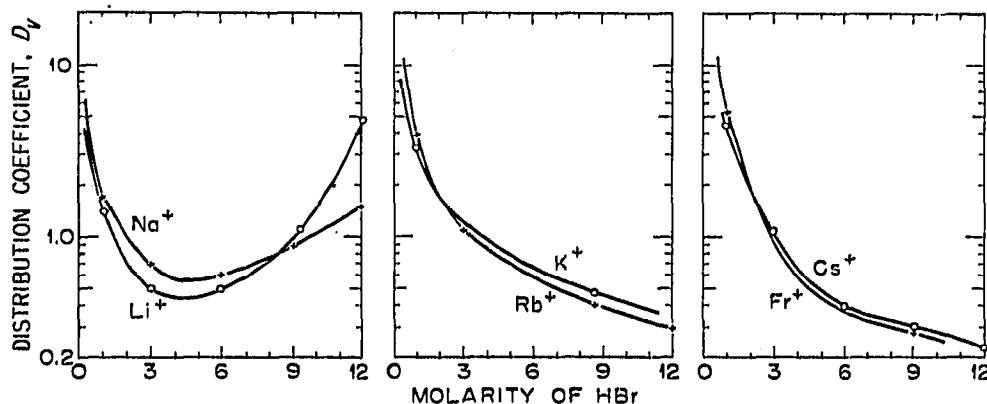

Fig. 1. Adsorption of alkali metals from HBr solutions (Dowex 50-X4, 25°).

In 12 M HBr solutions, column separation of Na^+ from the higher alkali metals should be possible. However, in 12 M HBr adsorbability of Na^+ is low ($D_v =$ *ca.* 1.5) and hence long columns would be needed for satisfactory separation of Na^+ from higher alkali metals. On the other hand, the separation factor, $D_v(Li^+)/D_v(Na^+)$, is 2.3 in 12 M HBr and Li^+ is sufficiently strongly adsorbed ($D_v = 4.8$) to permit its separation from Na^+ and the other alkali metals with relatively short columns. A typical separation is shown in Fig. 2. A 0.15 ml aliquot of o.1 M LiBr–o.1 M NaBr in 12 M HBr was added to a 0.28 cm² × 5 cm column of Dowex 50-X4 which had been
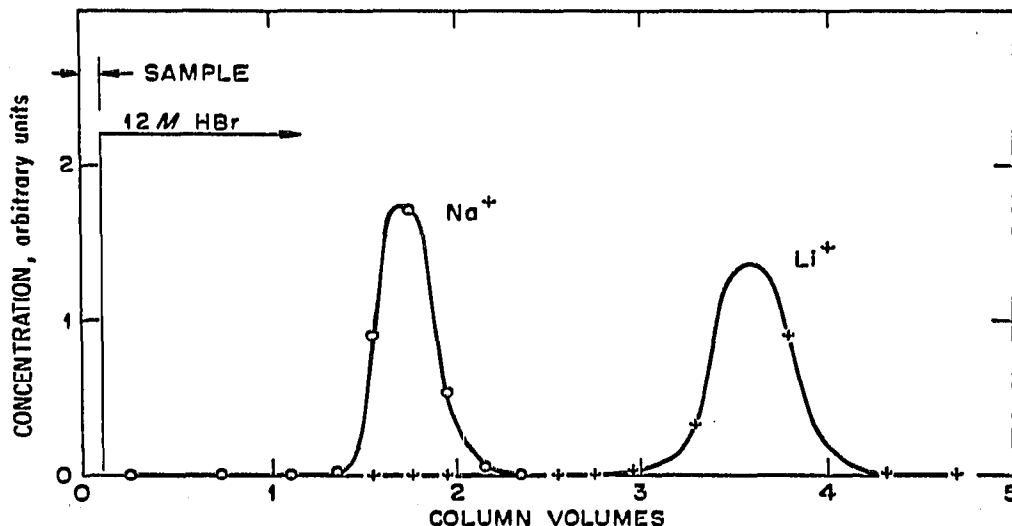

Fig. 2. Separation of Na^+ and Li^+ in 12 M HBr solution (Dowex 50-X4, 0.28 cm² × 5 cm column, 60°).

pretreated with 12 M HBr. On elution with 12 M HBr (at 60°), Na+ and Li+ appeared in the effluent as separate bands near 1.7 and 3.6 column volumes (c.v.), respectively.

(*b*) *Alkaline earths* (*Figs. 3, 4, 5, and 6*). These elements show marked differences in adsorbability at high M HBr (Fig. 3). Mg(II) and Be(II) are weakly adsorbed ($D_v < 1$) in the region 3 to 12 M HBr. Adsorption functions of Ca(II) and Sr(II) show minima near 5 M HBr where D_v is 1.1 and 1.5, respectively. Values of D_v then increase rapidly with further increase in HBr concentration and in 12 M HBr, $D_v >$ 10^2 for both elements. Adsorbability of Ba(II) decreases to a minimum $D_v = 3$ near 4 M HBr then increases slowly to $D_v = 16$ in 12 M HBr. At low M HBr, Ra(II) is slightly more strongly adsorbed than Ba(II); however, at high M HBr D_v(Ra) $< D_v$ (Ba). The adsorption function of Ra(II) goes through a minimum near 4 M HBr, exhibits a broad maximum ($D_v = 5.6$) near 9 M HBr and then decreases with increasing M HBr.
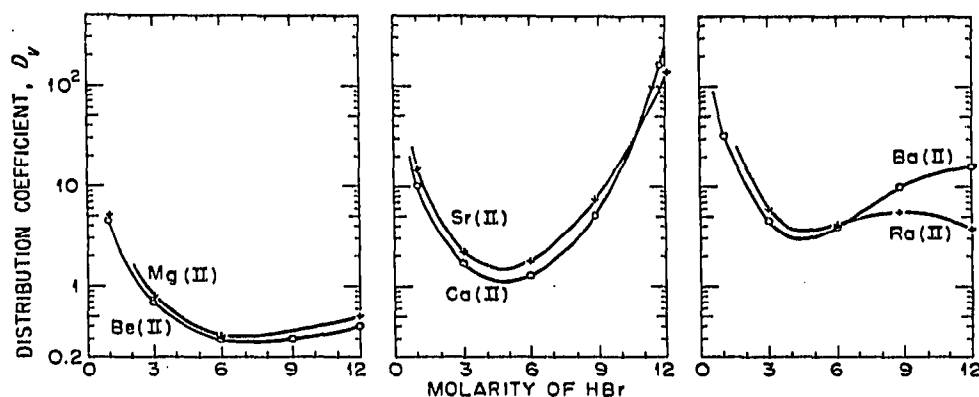

Fig. 3. Adsorption of alkaline earth elements from HBr solutions (Dowex 50-X4, 25°).

The strong adsorption of Ca(II) and Sr(II) relative to the lighter and heavier alkaline earth elements at high M HBr is not understood. In concentrated HCl and $HClO_4$ solutions, Ca(II) and Sr(II) are also more strongly adsorbed than the other alkaline earth elements. As pointed out earlier for the perchlorate system[2], strong adsorbability from high M perchloric acid solutions often occurs for elements whose perchlorate salts, at high salt concentrations, have high activity coefficients. The negligible adsorbability of Mg(II) relative to Ca(II) and Sr(II) in high M $HClO_4$ solutions thus seemed unexpected, since the activity coefficients of $Mg(ClO_4)_2$, at high concentrations, are even larger than the corresponding activity coefficients of $Ca(ClO_4)_2$ and $Sr(ClO_4)_2$. Low adsorbability of Mg(II) relative to Ca(II) and Sr(II) in HBr solutions (at high μ) likewise is unexpected since the activity coefficients of $MgBr_2$ at high concentrations are larger than the corresponding activity coefficients of $CaBr_2$ and $SrBr_2$.

More meaningful relationships between adsorption and activity coefficient functions might be found if the adsorption functions could be compared with activity coefficients of the trace metal salts in the appropriate acids. However, data for the latter are not available, particularly at high acid concentrations. It is interesting, nevertheless, that D_v values for Ca(II) in high M HCl, HBr and $HClO_4$ solutions also increase in the same order as the activity coefficients of concentrated Ca(II) salt solutions, *i.e.*, $\gamma_{\pm CaCl_2} < \gamma_{\pm CaBr_2} < \gamma_{\pm Ca(ClO_4)_2}$. D_v of Mg(II) in the same three acids

though low (see Table I) also increase in the same order as the activity coefficients of the corresponding Mg(II) salt solutions.

Adsorption functions of alkaline earth elements in HCl, HBr, and $HClO_4$ solutions also might be compared with the activity coefficients of the acids, since the activity coefficients of the trace metal salts might lie between those of the acids and the corresponding metal salt solutions. In Fig. 4, the adsorption functions of Ca(II) and Ba(II) in HCl, HBr, and $HClO_4$ solutions are compared with the activity coefficient functions of the acids. In the region ca. 6 to 12 M acid concentration, the adsorption functions of Ca(II) in the acids resemble the activity coefficient functions of the corresponding acids while the adsorption functions for Ba(II) do not. Thus, D_v for Ca(II) at a given acid concentration increases in the order, HCl < HBr < $HClO_4$, which is the order of the activity coefficients of the acids, while D_v for Ba(II) increases in the order, $HClO_4$ < HCl < HBr.

Hence, one cannot always predict the order of adsorption of elements from activity coefficient data for the acids alone. Nevertheless, as shown in subsequent sections (see e.g., Table I), when elements are adsorbed from high M HCl, HBr, and $HClO_4$ solutions, adsorbabilities usually increase in the same order as $\gamma_\pm$ of the acids.

Because of the large differences in adsorbability, some alkaline earths can easily be separated with small columns. For example, the separation factor, D_v Ca(II)/D_v Mg(II), in 12 M HBr is > 10^2 and still > 10 in 9 M HBr. At these HBr concentrations, Mg(II) is weakly adsorbed and thus may readily be separated from Ca(II) as illustrated in Fig. 5. A 0.1 ml sample containing 0.1 M $MgBr_2$, tracer $CaBr_2$ ([47]Ca–[47]Sc tracer) and 9 M HBr was added to a 0.25 cm² × 4 cm column of Dowex 50-X4 which had been pretreated with 9 M HBr. On elution (25°) with 9 M HBr, Mg(II) appeared in a sharp band within the first 2 c.v. while Ca(II) remained adsorbed; it was eluted with 4 M HBr. The [47]Sc daughter of the [47]Ca tracer remained adsorbed on the column during elution of Mg(II) and Ca(II). It may be rapidly eluted with 6 M HNO_3 or HCl–HF mixtures e.g. 4 M HCl–0.1 M HF.

A column separation involving all six alkaline earths is shown in Fig. 6. For this experiment, 0.1 ml of a 12 M HBr solution containing 0.05 M $MgBr_2$ and the tracers [7]Be, [47]Ca–[47]Sc, [85]Sr, [133]Ba, and [223]Ra, was added to a 0.25 cm² × 6 cm column of Dowex 50-X4 (20 to 30 μ particles, 60°) which had been pretreated with 12 M HBr. The [223]Ra tracer had been separated from its parent, [227]Ac and other members of the [227]Ac decay chain immediately before use by a cation exchange method described earlier[8]. On elution with 12 M HBr, the weakly adsorbed alkaline earths, Be(II) and Mg(II), appeared together in a single band near 1 c.v. On continued elution, Ra(II) and Ba(II) were removed in separate bands with peak maxima near 2.9 and 6.8 c.v., respectively. Ca(II) and Sr(II) were then removed together with ca. 3 c.v. of 5 M HBr. As in the previous separation, Sc(III) ([47]Sc) remained on the column.

(c) *Scandium(III), yttrium(III), rare earths(III), actinium(III), and trans-plutonium(III) elements (Figs. 7 and 8)*. Adsorbability of Sc(III) decreases to a minimum, $D_v = 4$, near 4 M HBr and then increases sharply with increasing M HBr to $D_v > 5 \cdot 10^3$ in 12 M HBr. The adsorption function of Y(III) resembles that of Sc(III), but at high HBr concentrations adsorbability is much lower. Adsorbability of Y(III) increases from a minimum $D_v = 1.4$ near 6 M HBr to $D_v = 23$ in 12 M HBr.

The adsorption functions of La(III) and Lu(III), the first and last members of the rare earth series, presumably define the region of maximum and minimum ad-
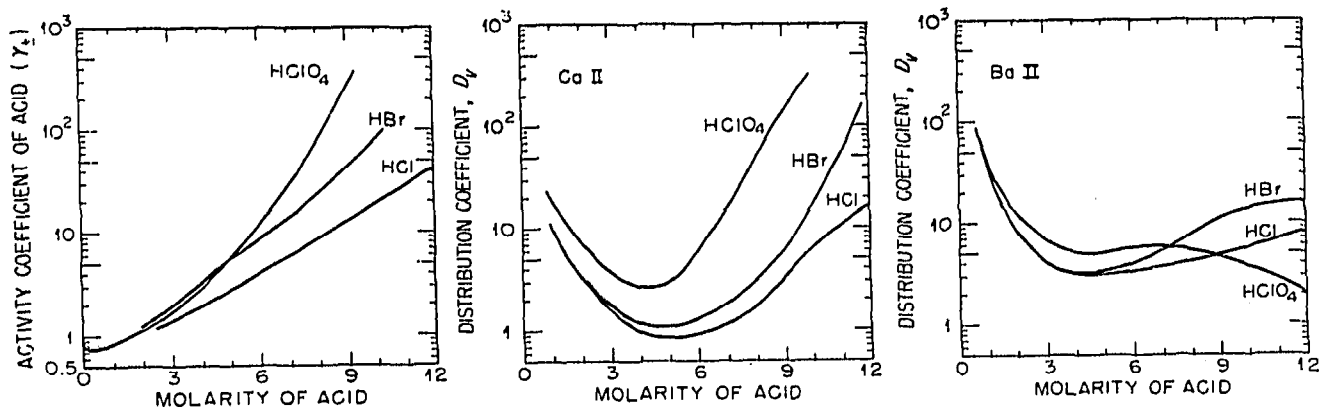
Fig. 4. Comparison of adsorption functions of Ca(II) and Ba(II) in HCl, HBr and HClO$_4$ solutions with activity coefficient functions of the acids.
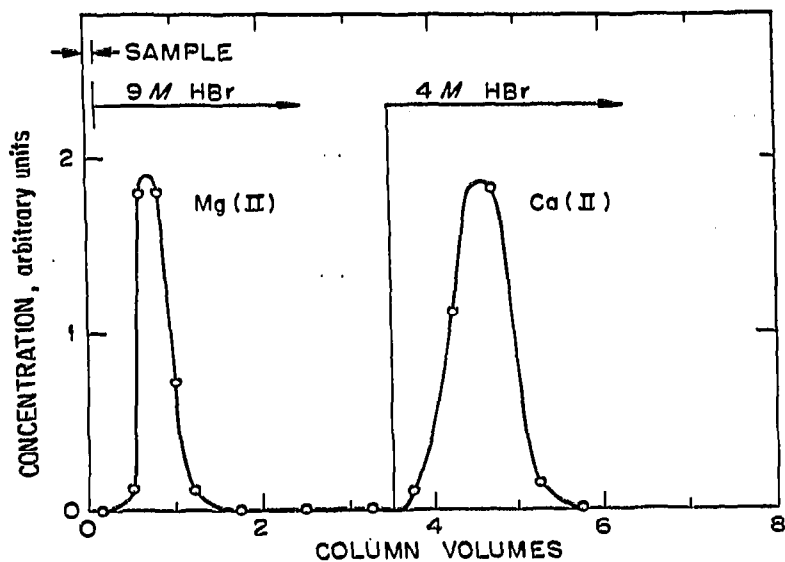

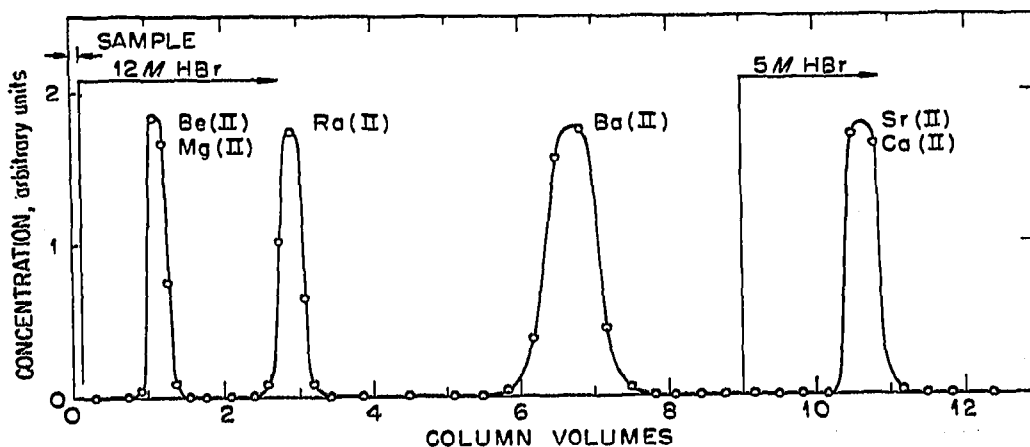Fig. 5. Separation of Mg(II) and Ca(II) in HBr solution (Dowex 50-X4, 0.25 cm^2 × 4 cm column, 25°).

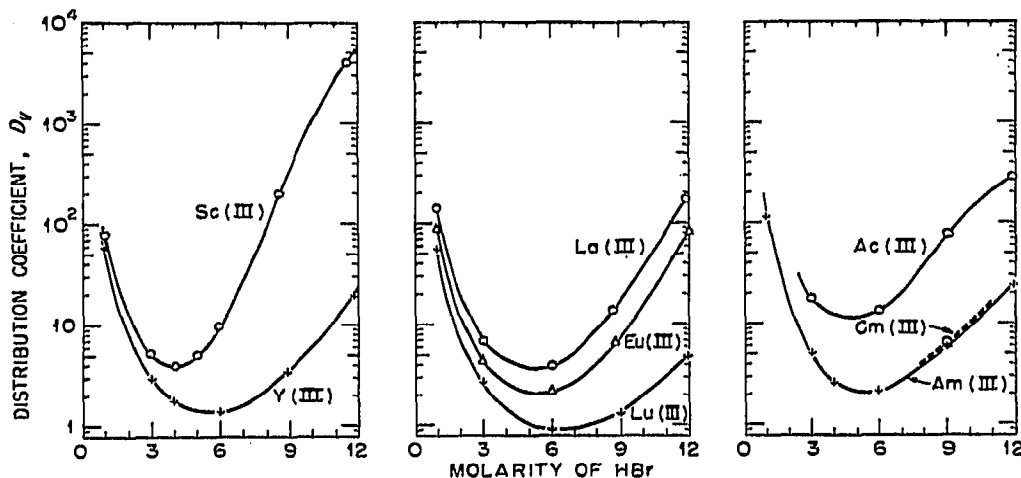Fig. 6. Separation of alkaline earths in HBr solutions (Dowex 50-X4, 0.25 cm^2 × 6 cm column, 60°.

Fig. 7. Adsorption of Sc(III), Y(III), R.E.(III) and some actinide(III) elements from HBr solutions (Dowex 50-X4, 25°).

sorbability for the R.E.(III) elements. The adsorption function of Eu(III), for example, lies between those for La(III) and Lu(III) as shown in Fig. 7. Adsorbabilities decrease with increasing HBr concentration to minima near 6 M HBr and then increase with increasing HBr concentration. Where comparisons are possible, i.e., for Eu(III), our data are in good agreement with similar measurements of CHOPPIN AND DINIUS[9].

At high acid concentrations, R.E.(III) elements are more strongly adsorbed from HBr solutions than from HCl solutions; however, they are more weakly adsorbed from HBr solutions than from $HClO_4$ solutions.

The trivalent actinide elements also exhibit adsorption minima in HBr solutions. These minima are more pronounced than those in HCl solutions[2,9-11] and at high acid concentrations values of D_v in HBr solutions are significantly larger than in HCl solutions. The adsorption functions for Ac(III) and Am(III) are given in Fig. 7 along with a single measurement (9 M HBr) for Cm(III). At high M HBr, Ac(III) is about ten times more strongly adsorbed than Am(III) or Cm(III), for which values of D_v are about the same. The adsorption function of Pu(III) (see section v) is similar to that of Am(III). Presumably the functions of other trivalent transplutonium elements also do not differ appreciably from that of Am(III).

The significant adsorbability of trivalent actinide and rare earth elements in relatively concentrated HBr solutions permits their separation from weakly adsorbed elements as illustrated in Fig. 8. A 0.2 ml sample containing actinide(III) tracers ([241]Am and [244]Cm), a rare earth(III) tracer ([155]Eu) and a weakly adsorbed element ([134]Cs) in 9 M HBr was added to a 0.28 cm² × 3 cm column of Dowex 50-X4 which had been pretreated with 9 M HBr. The column temperature was maintained at 60° to sharpen elution bands. At this temperature Am(III), Cm(III), and Eu(III) in 9 M HBr are slightly more strongly adsorbed than at 25°. On elution with 9 M HBr, Cs+ appeared in the first c.v. of effluent, Am(III) and Cm(III) were eluted together in a band with peak concentration near 8.3 c.v. and Eu(III) appeared in a slightly broader band with peak concentration near 10.5 c.v. Analysis of the Am–Cm effluent fractions by α-counting and γ-spectroscopy (to identify [241]Am) showed that Am(III) eluted slightly ahead of Cm(III).
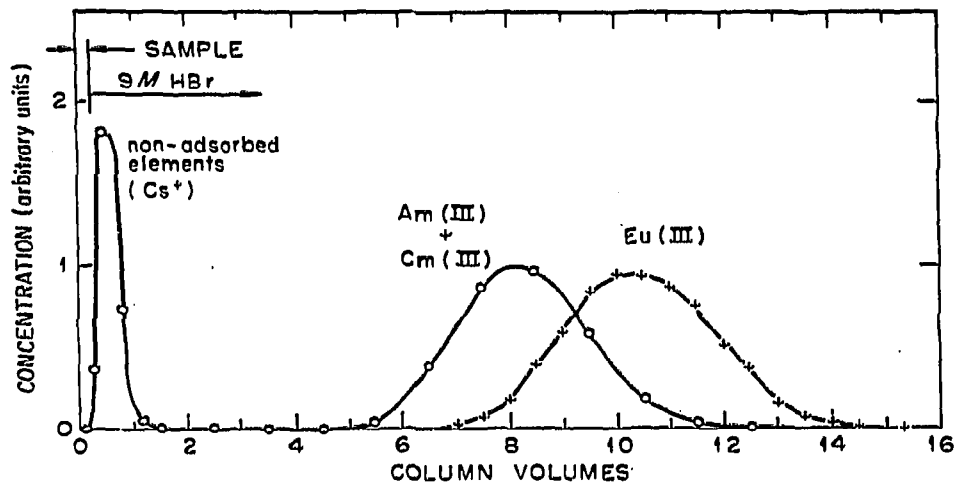
Fig. 8. Separation of some rare earth(III) and actinide(III) elements [Eu(III), Am(III),[Cm(III)] from weakly adsorbed elements (Cs$^+$) (Dowex 50-X4, 0.28 cm^3 × 3 cm column, 60°).
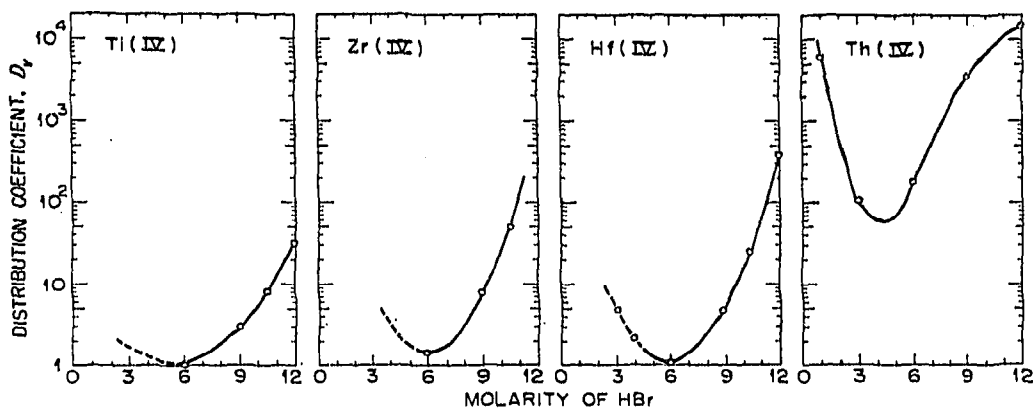

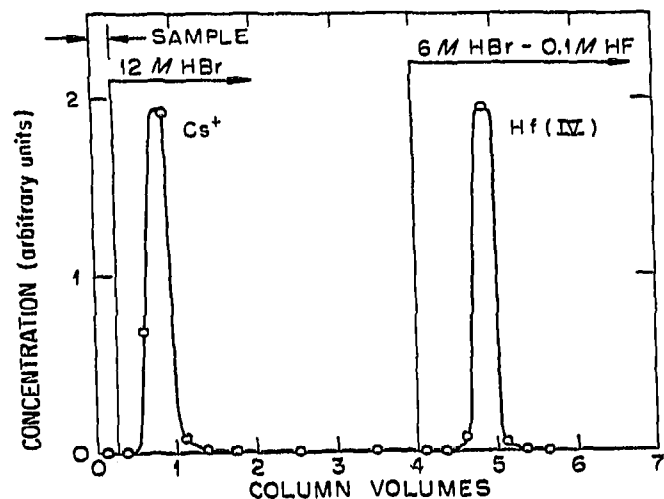Fig. 9. Adsorption of Ti(IV), Zr(IV), Hf(IV) and Th(IV) from HBr solutions (Dowex 50-X4,[25°).

Fig. 10. Separation of Cs$^+$ and Hf(IV) by cation exchange (Dowex 50-X4, 0.28 cm^3 × 4 cm column. 25°).

(d) *Titanium(IV), zirconium(IV), and hafnium(IV)* (*Figs. 9 and 10*). These elements show adsorption minima near 6 M HBr (Fig. 9) where adsorbabilities are low $(D_v \leqslant 1.5)$. Above 6 M HBr, adsorbabilities increase rapidly with increasing M HBr; in 12 M HBr D_v is *ca.* 30 for Ti(IV) and $> 10^2$ for Zr(IV) and Hf(IV). In dilute HBr solutions, adsorbabilities presumably increase with decreasing M HBr but no attempt was made to evaluate distribution coefficients for M HBr < 3, since, at these low acidities, hydrolytic reactions were expected to cause complications.

A typical separation of a weakly adsorbed element (Cs$^+$) from Hf(IV) is shown in Fig. 10; it is based on the strong adsorption of Hf(IV) from concentrated HBr solutions. A 0.25 ml sample containing tracers of Cs$^+$ and Hf(IV) in 12 M HBr was added to a 0.28 cm$^2 \times 4$ cm column which had been pretreated with 12 M HBr. On elution with 12 M HBr, Cs$^+$ was eluted in a sharp band with peak concentration near 0.8 c.v. while Hf(IV) was retained. The latter was eluted in a sharp band with 6 M HBr–0.1 M HF. While elution of Hf(IV) may also be effected with 6 M HBr, where adsorbability is at a minimum $(D_v = 1)$, Hf(IV) is more rapidly removed with HBr–HF mixtures since in these media, weakly adsorbed fluoride complexes presumably are formed.

(e) *Thorium(IV)* (*Fig. 9*). At no HBr concentration is adsorbability of Th(IV) low, although its adsorption function also shows a minimum. While D_v values are $\leqslant 1.5$ at the minima for Ti(IV), Zr(IV), and Hf(IV), $D_v = 60$ for Th(IV) at its minimum near 4 M HBr. In 12 M HBr, D_v for Th(IV) exceeds 10^4. The adsorption function of Th(IV) in HBr solutions resembles those in HCl and HClO$_4$ solutions[2] though at high acid concentrations, Th(IV) is much more strongly adsorbed from HClO$_4$, than from HCl or HBr solutions.

The high adsorbability of Th(IV) at all HBr concentrations may be used for numerous column separations of Th(IV) from more weakly adsorbed elements. Separation of Th(IV) (UX$_1$) from some other elements in 9 M HBr is described in section t (Fig. 26). Th(IV) may be eluted with appropriate complexing agents, *e.g.*, citrate media or HCl–HF mixtures; in the separation shown in Fig. 26, the latter was used.

(f) *Niobium(V), tantalum(V), and protactinium(V)* (*Fig. 11*). Since hydrolytic difficulties with these elements were anticipated at low and moderate HBr concentrations, adsorption behavior was not investigated below 9 M HBr. Even in 9 to 12 M HBr solutions, these elements tend to undergo irreversible hydrolytic reactions, and hence, lower limits of D_v could only be estimated. This was done by extrapolation of data obtained with tracers in HBr–HF mixtures in which media reversible exchange occurs. Adsorbabilities of Nb(V), Ta(V), and Pa(V) in high M HBr solutions decrease with increasing HF concentration in the region *ca.* 10^{-3} to 0.2 M HF. Values of D_v at the lowest HF concentration presumably represent lower limits of adsorbability.

In 9 M HBr—*ca.* 10^{-3} M HF, D_v is 3, > 10 and > 15 for Nb(V), Ta(V), and Pa(V), respectively, while in 12 M HBr—*ca.* 10^{-3} M HF, D_v is 8, > 20 and $> 10^2$, respectively, for these same elements. Thus, although the adsorption functions were not determined precisely, adsorbabilities of Nb(V), Ta(V), and Pa(V) appear to increase sharply with increasing M HBr in the region 9 to 12 M HBr; presumably adsorption minima occur at HBr concentrations < 9 M.

The adsorption behavior of Nb(V) in high M HBr–low M HF solutions differs considerably from that of Ta(V) and Pa(V). In 9 or 12 M HBr solutions containing

10^{-3} to 10^{-2} M HF, adsorbabilities of Ta(V) and Pa(V) increase sharply with decreasing M HF while adsorbability of Nb(V) tends to reach an asymptote.

In 9–12 M HBr solutions containing > 0.2 M HF, Nb(V), Ta(V), and Pa(V) are weakly adsorbed (D_v < 1) hence these media are effective eluting agents for these elements.

A cation exchange separation of Nb(V) tracer from some weakly adsorbed radioactive impurities initially present in the ^{95}Nb tracer used is shown in Fig. 11. This separation is based on the significant adsorbability of Nb(V) in 12 M HBr solutions containing relatively small amounts of HF. A 0.10 ml aliquot of ^{95}Nb in 12 M HBr–0.05 M HF was added to a 0.13 cm^2 × 4 cm column of Dowex 50-X4
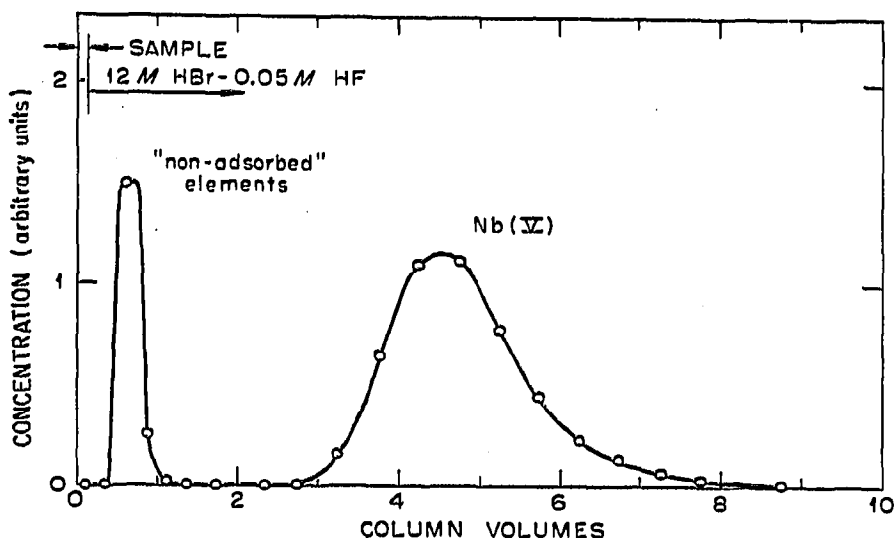

Fig. 11. Separation of Nb(V) and non-adsorbed elements by cation exchange (Dowex 50-X4, 0.13 cm^2 × 4 cm column, 60°).

resin (60°) which had been pretreated with the same acid mixture. On elution with 12 M HBr–0.05 M HF, the radioactive impurity or impurities (unidentified) appeared in the effluent in a band with maximum concentration near 0.6 c.v. while Nb(V) eluted in a sharp band near 4 c.v. Since few elements are expected to elute in HBr–HF media exactly like Nb(V), the separation of Fig. 11 should provide a convenient method for purifying ^{95}Nb tracer.

(g) *Molybdenum(VI) and tungsten(VI) (Figs. 12 and 13)*. These elements are slightly adsorbed from high M HBr (Fig. 12); their adsorption behavior was not investigated at HBr concentrations less than *ca.* 6 M because of expected hydrolytic difficulties. Low adsorbability has been reported[7] for Mo(VI) in 0.5 M HBr solutions, however. Adsorbability of Mo(VI) reaches a maximum (D_v = 4.6) near 9 M HBr. W(VI) is weakly adsorbed in *ca.* 6 to 12 M HBr solution; in this region of HBr concentration adsorbability increases slightly with increasing M HBr and in 12 M HBr, D_v = 1.1.

A separation of W(VI) from Mo(VI) in 9 M HBr is illustrated in Fig. 13; it is based on the slightly lower adsorbability of W(VI) relative to Mo(VI) in this medium. A 0.1 ml sample containing 0.01 M Mo(VI), 10^{-5} M W(VI) and 9 M HBr was added to a 0.2 cm^2 × 6 cm column of Dowex 50-X4 (60°) which had been pretreated with 9
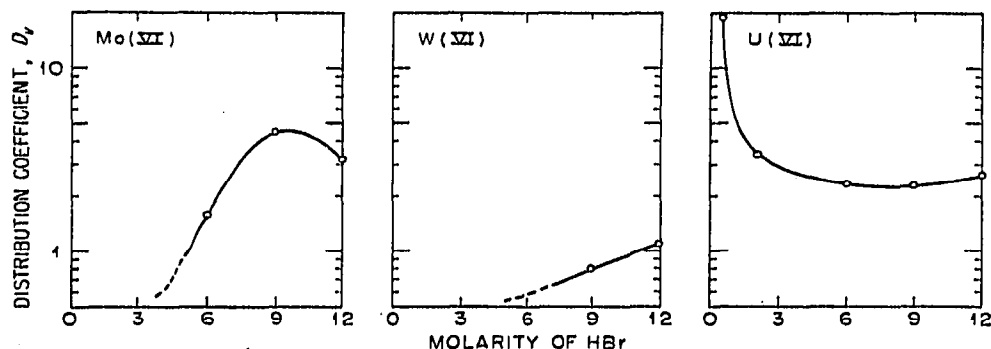
Fig. 12. Adsorption of Mo(VI), W(VI) and U(VI) from HBr solutions (Dowex 50-X4, 25°).

M HBr. On elution with 9 M HBr, W(VI) and Mo(VI) appeared in the effluent in separate elution bands with maximum concentrations at 1.3 and 2.9 c.v., respectively.

The separation factor $D_v(\text{Mo(VI)})/D_v(\text{W(VI)})$ is *ca.* 2.9 at 60° and 5.7 at 25°; separation of W(VI) from Mo(VI) should thus be more favorable at low temperatures provided low flow rates and a fine mesh resin are used to avoid broadening and hence, overlap of the W(VI) and Mo(VI) elution bands.

(*h*) *Vanadium(IV), chromium(III) and manganese(II)*. Distribution coefficients of V(IV) and Mn(II) decrease with increasing M HBr. Adsorbability of V(IV) and Mn(II) becomes negligible ($D_v < 1$) above *ca.* 3 and 1 M HBr, respectively.
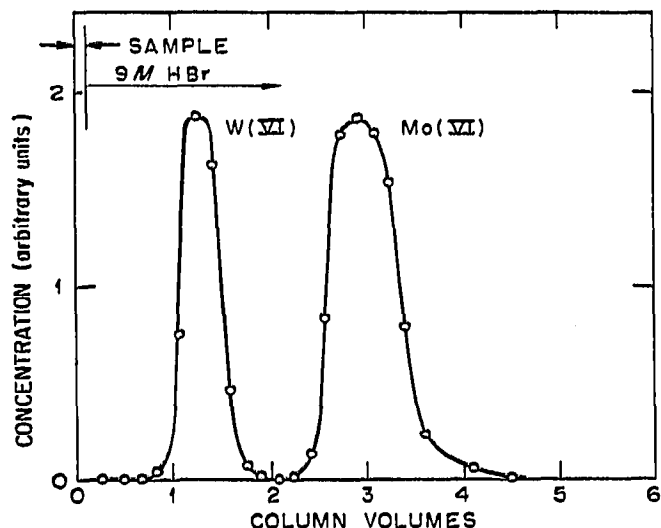

Fig. 13. Separation of W(VI) and Mo(VI) by cation exchange (Dowex 50-X4, 0.2 cm² × 6 cm column, 60°).

D_v values for Cr(III) were measured with stock solutions which had been heated to assure that Cr(III) bromide complexes would form. Adsorption of Cr(III) from these solutions is negligible in the region 6 to 12 M HBr. Adsorption of Cr(III) from dilute HBr solutions was not studied; however, strong and quantitative adsorption of Cr(III) from dilute HBr solutions (0.5 M) has been reported[7].

(*i*) *Technetium(VII) and rhenium(VII)*. Adsorbabilities of Tc(VII) and Re(VII) were measured with stock solutions of Tc(VII) and Re(VII) in 3 to 12 M HBr solutions which initially contained small amounts of bromine as oxidizing agent. When aliquots

of these solutions were added to the columns, bromine was adsorbed by the resin, and partial reduction of Tc(VII) and Re(VII) apparently occurred.

In a typical experiment, tracer [186]Re, initially in the VII state, was added to a small column and elution carried out with 6 M HBr. Two distinct elution bands were observed with peak concentrations near 0.7 and 1.7 c.v. Presumably the first band contained rhenium in a reduced form (ReBr$_6{}^{2-}$?) while the second is characteristic of the (VII) state. Two elution bands were also observed at other HBr concentrations. On the assumption that the more strongly adsorbed species is Re(VII), D_v of Re(VII) apparently increases from 0.8 near 3 M HBr to 1.8 in 12 M HBr.

The adsorption function of Tc(VII) roughly parallels that of Re(VII), though adsorbabilities are lower. In 12 M HBr, D_v for Tc(VII) is 1.2; in 3 M HBr, $D_v < 1$. As with Re(VII), "splitting" of the technetium band occurs, presumably because of partial reduction of Tc(VII) to a negligibly adsorbed lower oxidation state (TcBr$_6{}^{2-}$?). Reduction of Tc(VII) in high M HBr solutions has also been observed by others in paper chromatographic experiments[12]. Heating Tc(VII) in high M HBr solution for several minutes has also been reported[12] to cause essentially complete reduction to Tc(IV) (TcBr$_6{}^{2-}$).

(j) Platinum elements. The platinum elements in HBr solutions form very stable bromide complexes which, in general, are only weakly adsorbed by cation exchangers. Low adsorbability ($D_v < 1.5$) in the region 0.5 to 12 M HBr was confirmed for Ru(IV), Os(IV), Rh(III), Ir(III), Ir(IV), and Pt(IV); these elements presumably were present as the hexabromo complexes, MBr$_6{}^{2-}$ or MBr$_6{}^{3-}$. Low adsorbability was also confirmed for Pd(II) (PdBr$_4{}^{2-}$).

Under some conditions, however, some platinum elements, particularly Ru(IV), Os(IV), and Rh(III), are partially adsorbed from strong HBr solutions. The adsorbed species presumably are slowly reversible, hydrated or hydrolyzed cationic species[13] which have not been completely converted to the higher bromide complexes. If samples are heated several hours in concentrated HBr before adding them to the columns, the amount which adsorbs is markedly reduced.

Conversion of Os(IV) to weakly adsorbed bromide complexes was particularly slow under the conditions of our experiments. Preheating osmium samples prepared by reduction of OsO$_4$ in 9 M HBr for as long as six hours did not convert the Os(IV) species completely to the weakly adsorbed (hexa?) bromide species.

(k) Cobalt(II), nickel(II) and copper(II). In 0.1 M HBr solutions, these elements are strongly adsorbed; in 1 M HBr solution, Co(II), Ni(II), and Cu(II) are slightly adsorbed with $D_v = ca.$ 6, 4, and 5, respectively. Adsorbability becomes negligible above *ca.* 3 M HBr.

(l) Zinc(II), cadmium(II) and mercury(II). These elements are strongly adsorbed from very dilute HBr solutions. Adsorbability decreases rapidly with increasing M HBr and distribution coefficients become less than unity near 2, 0.5 and < 0.1 M HBr for Zn(II), Cd(II), and Hg(II), respectively. Our adsorption data for these elements at low M HBr are in good agreement with similar data of FRITZ AND GARRALDA[7]. The differences in adsorbability of Zn(II), Cd(II) and Hg(II) are sufficiently large to permit their separation from each other with dilute HBr solutions.

(m) Aluminum(III), gallium(III), indium(III) and thallium(III) (Figs. 14, 15 and 16). Adsorption functions of these elements are compared in Fig. 14. Adsorbability of Al(III) decreases with increasing M HBr to $D_v = ca.$ 1 near 3 M HBr; above 3 M HBr, D_v is < 1.
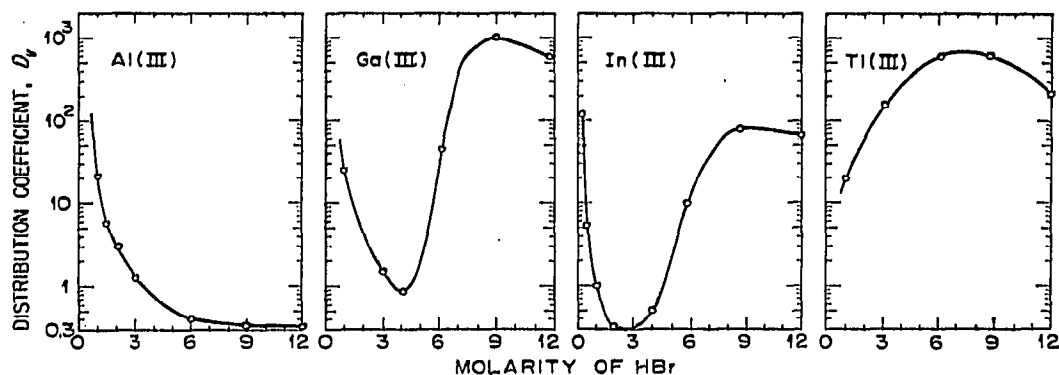
Fig. 14. Adsorption of Al(III), Ga(III), In(III) and Tl(III) from HBr solutions (Dowex 50-X4, 25°).

Adsorbability of Ga(III) increases sharply from a minimum $D_v = 0.9$ near 4 M HBr to $D_v = 10^3$ near 9 M HBr; D_v decreases slightly with further increase of M HBr. Similar results have been reported by others[14] for the adsorption of Ga(III) on a similar cation exchange resin in HBr solutions. Adsorption behavior of Ga(III) in HBr solutions thus closely resembles its adsorption behavior in HCl solutions[2,15], although at high M, D_v values are larger in HBr solutions than in HCl solutions of the same concentration.

In high M HCl and HBr solutions, Ga(III) is adsorbed by cation exchangers presumably as the negative species, $GaCl_4^-$ and $GaBr_4^-$, respectively. This assumption appears reasonable for reasons discussed earlier[16,15].

Adsorbability of In(III) increases rapidly from its minimum $D_v = 0.3$ near 3 M HBr to $D_v = 80$ near 9 M HBr; D_v decreases slightly with further increase in M HBr. Presumably, In(III) adsorbs as $InBr_4^-$ at high HBr concentrations. The adsorption behavior of In(III) in concentrated HCl solutions is markedly different; above ca. 1 M HCl, adsorption of In(III) is negligible[2]. One is tempted to conclude from the adsorption behavior of Ga(III) that failure of In(III) to adsorb significantly from high M HCl solutions implies that $InCl_4^-$ is not formed to an appreciable extent
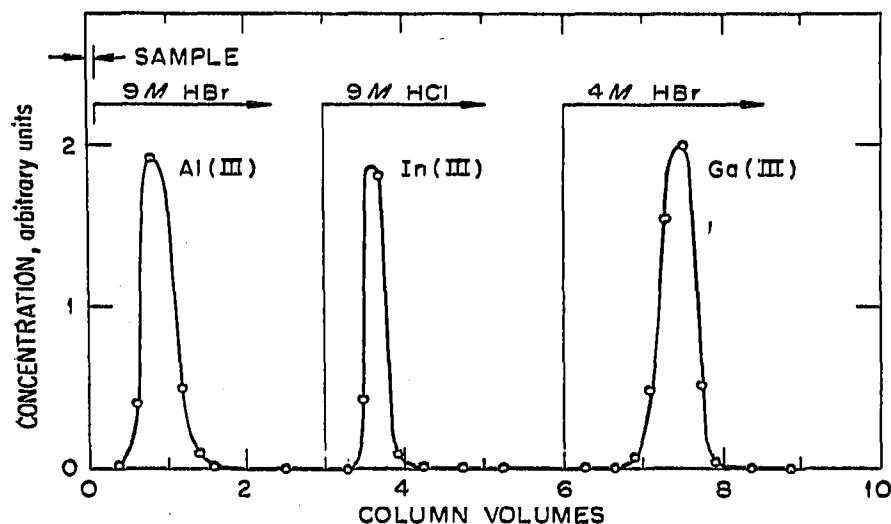

Fig. 15. Separation of Al(III), In(III) and Ga(III) by cation exchange (Dowex 50-X4, 0.25 cm³ × 4 cm column, 25°).

in concentrated HCl solutions; this would be in disagreement with the conclusions of others[17,18] who postulated from solvent extraction data that $InCl_4^-$ predominates in these media. We believe that higher complexes, $InCl_5^{2-}$ and $InCl_6^{3-}$, predominate.

Adsorbability of Tl(III) increases from $D_v = 20$ at 1 M HBr to a maximum $D_v = 700$ near 7 M HBr and then decreases to $D_v = 220$ at 12 M HBr. As with In(III), values of D_v for Tl(III) in high M HBr solutions are significantly larger than in corresponding HCl solutions. Below ca. 6 M HCl or HBr, adsorbability of Tl(III) decreases with decreasing acid concentration; presumably an adsorption minimum occurs at HCl and HBr concentrations $\ll$ 1 M.

The relatively high adsorbabilities of In(III), Ga(III), and Tl(III) at high M HBr permit their separation, individually, or as a group from Al(III) and other weakly adsorbed elements. After separation from weakly adsorbed elements, resolution of the adsorbed elements may be accomplished with other eluting agents as illustrated in Figs. 15 and 16.
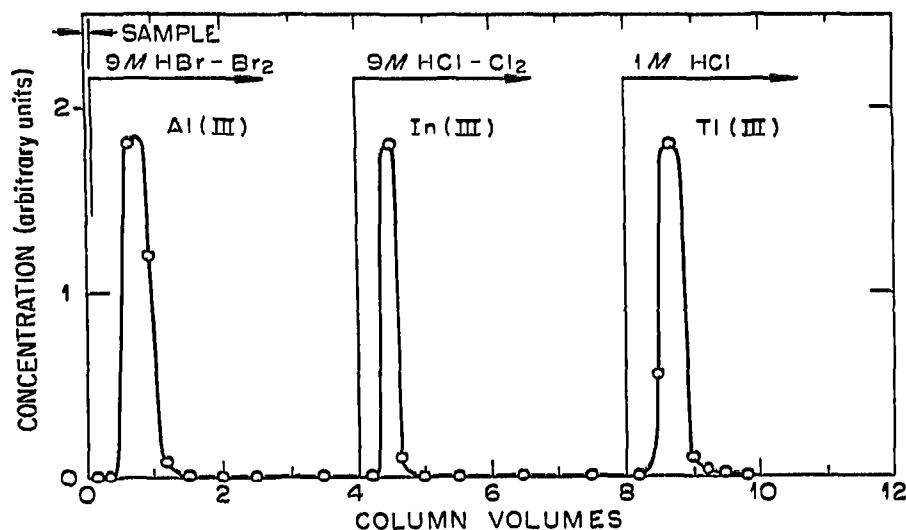

Fig. 16. Separation of Al(III), In(III) and Tl(III) by cation exchange (Dowex 50-X4, 0.2 cm² × 4 cm, column, 60°).

For the separation shown in Fig. 15, a 0.1 ml sample containing 0.1 M Al(III), trace concentrations of In(III) and Ga(III) and 9 M HBr was added to a 0.25 cm² × 4 cm column of Dowex 50-X4 which had been pretreated with 9 M HBr. Elution with 9 M HBr removed Al(III) in a sharp band with peak concentration near 0.8 c.v.; In(III) was removed with 9 M HCl. Ga(III) was then eluted in a sharp band with 4 M HBr, where D_v of Ga(III) is low. Satisfactory removal of Ga(III) could also have been achieved with 3 M HCl.

For the separation shown in Fig. 16, a 1 ml sample containing 0.02 M Al(III), 10^{-3} M Tl(III) and trace In(III) in 9 M HBr was evaporated to near dryness. The sample was taken up in ca. 0.05 ml of 9 M HBr–Br₂ solution and warmed slightly to assure oxidation of Tl(I) to Tl(III). The sample was added to a 0.2 cm² × 4 cm column of Dowex 50-X4 (60°) pretreated with 9 M HBr–Br₂ solution. On elution with the same solution, Al(III) was eluted in a sharp band with peak concentration near 0.9 c.v.; In(III) was eluted with 9 M HCl (containing Cl₂) and Tl(III) was removed with 1 M HCl, in which medium its adsorbability is low.

(n) *Iron(III)* (*Figs. 17 and 18*). The adsorption function of Fe(III) resembles those of Ga(III) and In(III) in HBr solutions. Adsorbability of Fe(III) decreases to a minimum $D_v = 1$ near 2 M HBr then increases sharply to a maximum $D_v = 2.5 \times 10^4$ near 8.5 M HBr; adsorbability decreases slightly with further increase of M HBr.
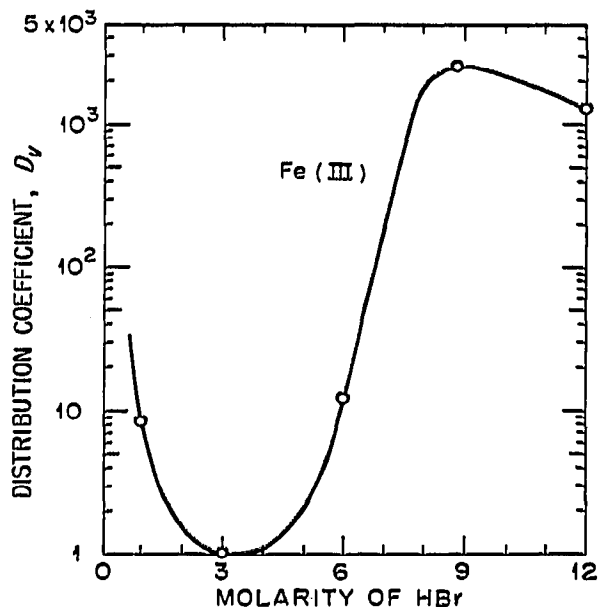

Fig. 17. Adsorption of Fe(III) from HBr solutions (Dowex 50-X4, 25°).

Like Ga(III), In(III), and Tl(III), Fe(III) presumably is adsorbed from high M HBr solutions as a negative complex (MBr_4^-). Recent measurements[19] of the absorption spectra of Fe(III) adsorbed on Dowex 50 in strong HBr and LiBr solutions lend further support to this conclusion.

At high M HBr, adsorbability of Fe(III) falls off rapidly with loading of the resin, and it is difficult to adsorb Fe(III) from 9 to 12 M HBr solutions when loading of the resin exceeds *ca.* 0.3 moles Fe(III) per liter bed. Hence, separations involving Fe(III) in high M HBr solutions are better when the concentration of Fe(III) is low. A similar rapid decrease in adsorbability with resin loading was observed for Fe(III) and Au(III) in concentrated chloride solutions[15] and for In(III) in concentrated iodide solutions[20]. Such abnormally rapid decreases in adsorbability with loading do not occur with elements which are adsorbed as cationic species, *e.g.*, R.E.(III) elements; the phenomenon, while not understood, seems to occur only with elements which presumably adsorb as negative species. Column separations involving these elements are thus less effective when the metal concentrations are high since large columns must be used to provide sufficient adsorptive capacity.

A typical separation of Fe(III) from several weakly adsorbed elements (Mn(II), Co(II), Cr(III), and V(IV)) in 9 M HBr is shown in Fig. 18. A *ca.* 0.3 ml sample containing 0.15 M Mn(II), 0.1 M Co(II), 0.1 M Cr(III), 0.1 M V(IV), and 0.01 M Fe(III) in 9 M HBr was added to a 0.28 cm² × 3 cm column of Dowex 50-X4. The sample had been heated several minutes to assure that nonadsorbable Cr(III) bromide complexes would form. The column had been pretreated with 9 M HBr. On elution with this same acid, Mn(II), Co(II), Cr(III), and V(IV) appeared in the first few column
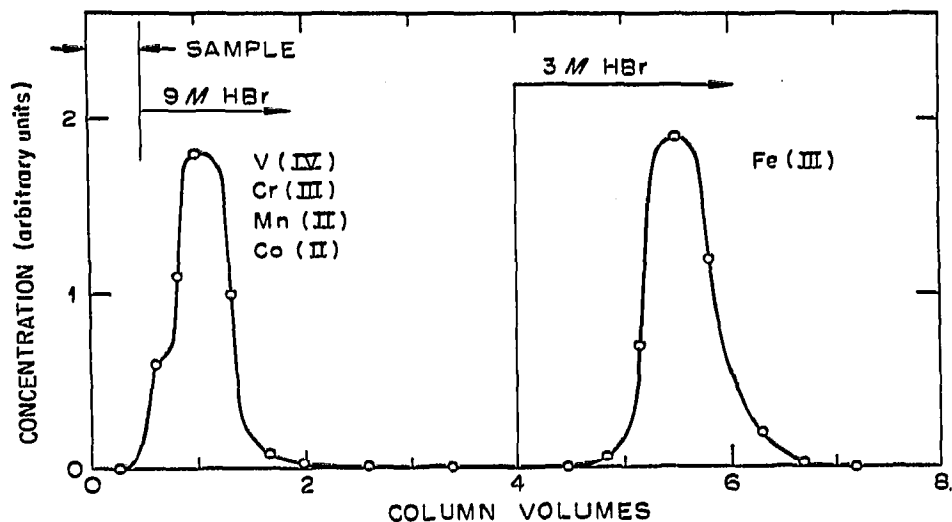
Fig. 18. Separation of Fe(III) from a number of metals by cation exchange (Dowex 50-X4, 0.28 cm^2 × 3 cm column, 25°).

volumes of effluent while Fe(III) adsorbed. Removal of Fe(III) was effected with 3 M HBr.

(o) *Gold(III) and silver(I)* (*Figs. 19 and 20*). The adsorption function of Au(III) resembles that of Tl(III). Adsorbability of Au(III) is low in dilute HBr solutions; it increases from $D_v = 10$ near 2 M HBr to a maximum $D_v = 10^2$ near 9 M HBr beyond which D_v slowly decreases with increasing M HBr. Presumably Au(III) adsorbs as the species, AuBr$_4^-$.

Adsorbability of Ag(I) is negligible in the range 0.2 to 12 M HBr. The low adsorbability of Ag(I) relative to Au(III) in high M HBr solutions permits its separation from Au(III). In addition, Ag(I) is much more soluble in concentrated HBr than
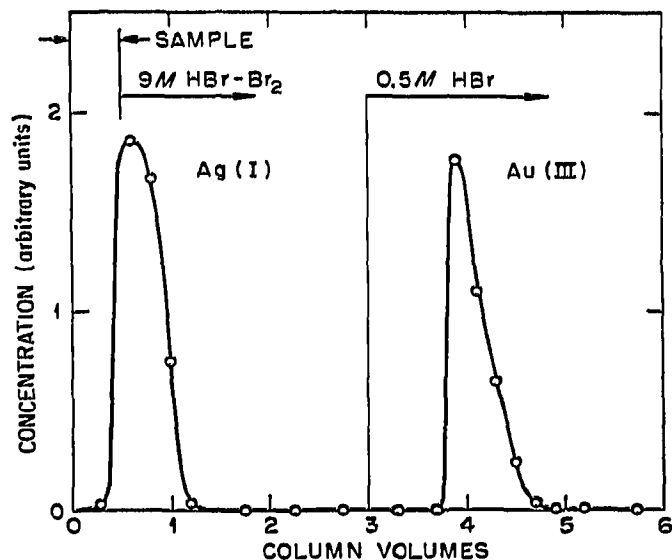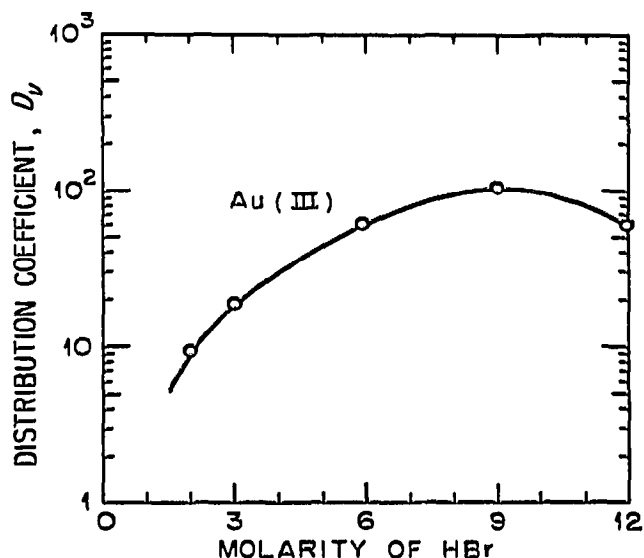

Fig. 19. Adsorption of Au(III) from HBr solutions (Dowex 50-X4, 25°).

Fig. 20. Separation of Ag(I) and Au(III) by cation exchange (Dowex 50-X4, 0.2 cm^2 × 5 cm column, 60°).

in dilute HBr and, as illustrated in Fig. 20, moderately high concentrations of Ag(I) may be separated. A 0.5 ml sample containing 0.05 M Ag(I), 0.01 M Au(III) and 9 M HBr was added to a 0.2 cm^2 × 5 cm column of Dowex 50-X4 which had been pretreated with 9 M HBr–Br$_2$ solution; the Br$_2$ was present to prevent possible reduction of Au(III) by the resin to metallic Au. On elution with 9 M HBr–Br$_2$ (60°), Ag(I) was eluted within approximately the first column volume of effluent while Au(III) was retained. Elution of Au(III) was effected with 0.5 M HBr solution.
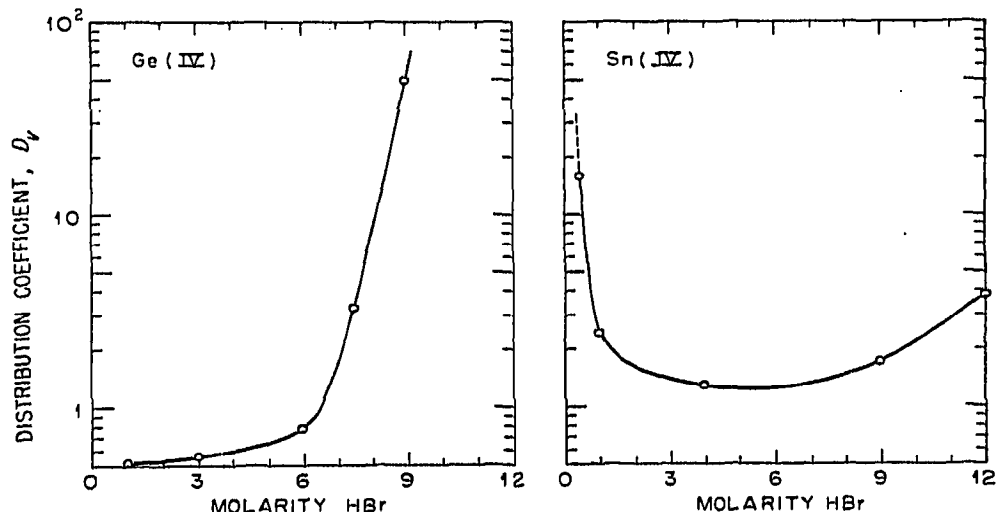

Fig. 21. Adsorption of Ge(IV) and Sn(IV) from HBr solutions (Dowex 50-X4, 25°).

(p) *Germanium(IV) and tin(IV) (Figs. 21 and 22).* Adsorbability of Ge(IV) is low ($D_v < 1$) in the region 1 to 6 M HBr. Significant adsorption of Ge(IV) begins near 7.5 M HBr ($D_v = 3.3$) and increases rapidly to $D_v = 50$ near 9 M HBr. Above 9 M HBr, adsorbability appears to increase with increasing M HBr; however, equilibration experiments were irreproducible because of serious losses of Ge(IV) (as volatile GeBr$_4$) from the solutions.

Adsorbability of Sn(IV) decreases from $D_v = 16$ at 0.5 M HBr to a minimum, $D_v = 1.3$ near 4 M HBr; then increases to $D_v = 3.8$ in 12 M HBr. Adsorbability of Sn(IV) at high M HBr, though low, is sufficient to permit its separation from non-adsorbed elements, e.g., Cd(II), as illustrated in Fig. 22. A 0.1 ml sample containing Cd(II), In(III), and Sn(IV) in 12 M HBr was added to a 0.28 cm^2 × 4 cm column of Dowex 50-X4 (60°) which had been pretreated with 12 M HBr. On elution with 12 M HBr, Cd(II), and Sn(IV) appeared in the effluent in separate elution bands with peak concentrations at 0.7 and 2.4 c.v., respectively, while In(III) remained adsorbed. In(III) was eluted with 2 M HBr, a medium in which adsorbability is low (Fig. 14). In 12 M HBr, Sn(IV) is slightly less adsorbed at 60° than at 25° and its elution bands are much sharper; hence elution of Sn(IV) at elevated temperatures is preferred.

(q) *Selenium(IV), tellurium(IV), and polonium(IV) (Figs. 23, 24, and 25).* Adsorbabilities of these elements are low at low M HBr and increase with increasing M HBr. At 12 M HBr, values of D_v for Se(IV), Te(IV), and Po(IV) are 1.8, 5.3 and 18, respectively.

Adsorbabilities of Te(IV) and Po(IV) in strong HBr solutions are sufficiently large to permit their separation from Se(IV) and other weakly adsorbed elements.
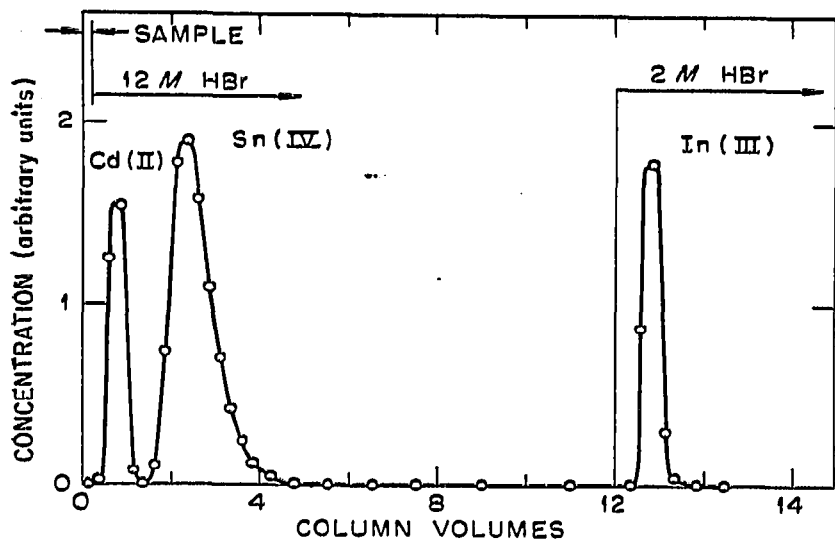
Fig. 22. Separation of Cd(II), Sn(IV) and In(III) by cation exchange (Dowex 50-X4, 0.28 cm² × 4 cm column, 60°).
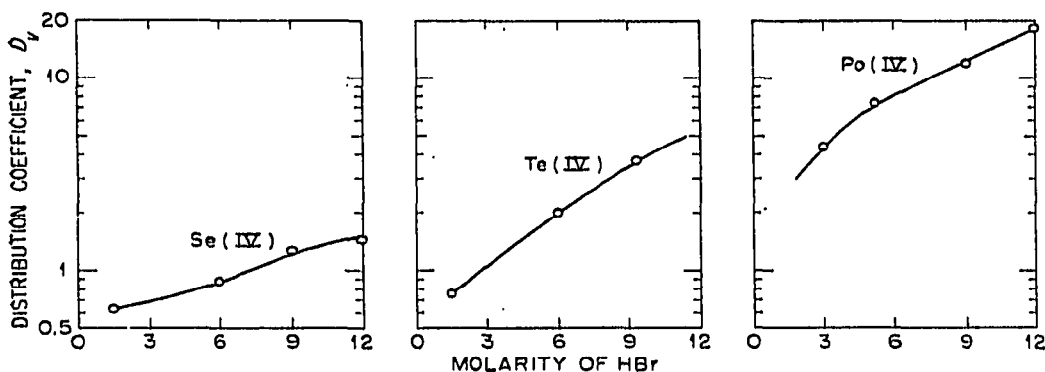

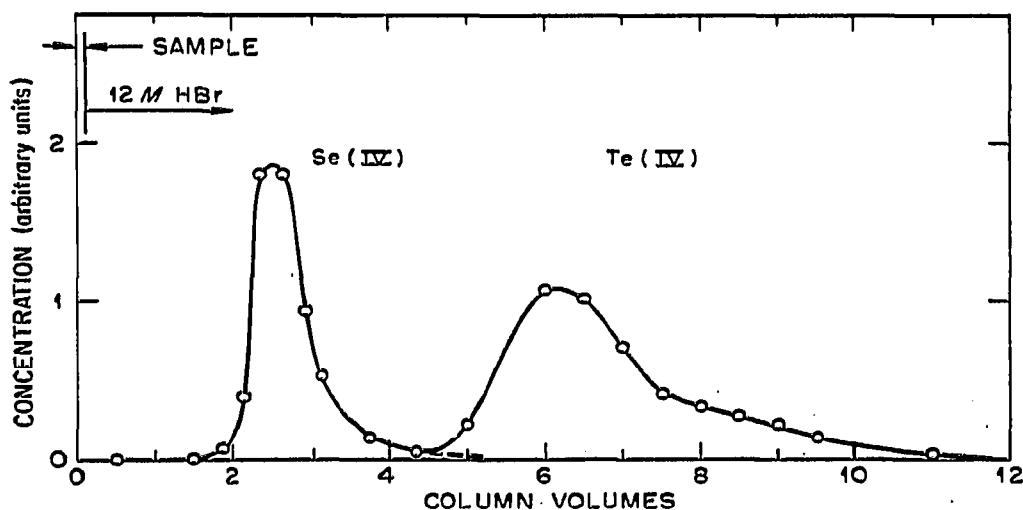Fig. 23. Adsorption of Se(IV), Te(IV) and Po(IV) from HBr solutions (Dowex 50-X4, 25°).

Fig. 24. Separation of Sc(IV) and Te(IV) by cation exchange (Dowex 50-X4, 0.2 cm² × 5 cm column, 25°).

A separation of Se(IV) from Te(IV) in 12 M HBr is shown in Fig. 24 and a separation of Po(IV) (RaF) from Bi(III) (RaE) and Pb(II) (RaD) is shown in Fig. 25.

For the separation shown in Fig. 24, a 0.1 ml sample containing Se(IV) and Te(IV) in 12 M HBr was added to a 0.2 cm² × 5 cm column of Dowex 50-X4 which had been pretreated with 12 M HBr. On elution (25°) with 12 M HBr, Se(IV) and
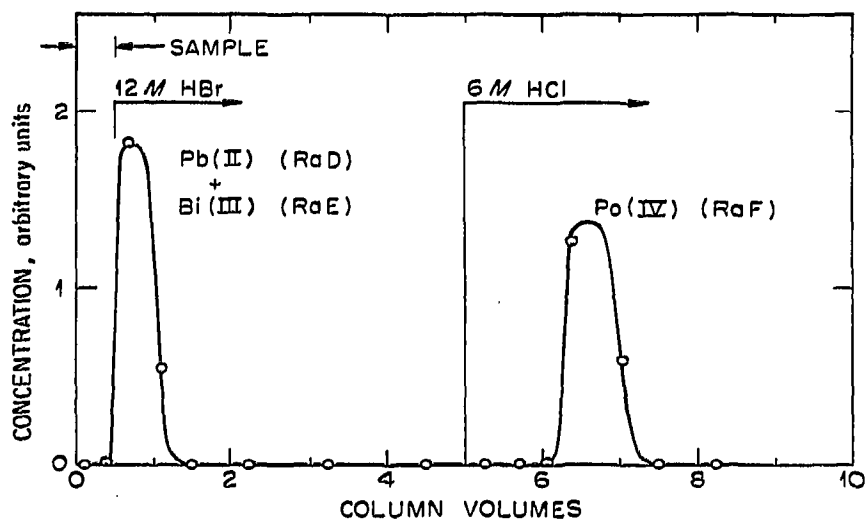

Fig. 25. Separation of Pb(II), Bi(III) and Po(IV) by cation exchange (Dowex 50-X4, 0.28 cm² × 3 cm column, 60°).

Te(IV) appeared in separate, though rather broad, elution bands with peak concentrations near 2.5 and 6.2 c.v., respectively. Sharper elution bands are observed for Se(IV) and Te(IV) when the separation is performed at 60°; however, both elements are less strongly adsorbed. For example, D_v of Te(IV) decreases from 5.7 at 25° to 3.4 at 60°; D_v for Se(IV) decreases from 2.0 to 1.5 in the same temperature interval.

For the separation shown in Fig. 25, a small aliquot of a 4 M HNO₃ solution containing ²¹⁰Po in secular equilibrium with its daughters, ²¹⁰Bi and ²¹⁰Pb, was evaporated with 1 ml of 9 M HBr to a volume of ca. 0.05 ml. The sample was taken up in 0.5 ml of 12 M HBr and added to a 0.28 cm² × 3 cm column of Dowex 50-X4 which had been pretreated with 12 M HBr. On elution with 12 M HBr (at 60°), Pb(II) and Bi(III) appeared immediately in the effluent essentially nonadsorbed while Po(IV) was retained. Po(IV) was removed with 6 M HCl in which medium its adsorbability is low[2,21].

Conversion of the Po(IV) species in HNO₃ solution to adsorbable bromide complexes is slow at room temperature. In a typical experiment in which a solution of Po(IV) tracer in HNO₃ solution was diluted with excess 9 M HBr at room temperature, added to a Dowex 50-X4 column, and eluted with 9 M HBr most of the Po(IV) appeared in the first column volume of effluent. However, when the Po(IV) solution was heated with 9 M HBr for a few minutes before adding it to the column, quantitative adsorption occurred[22].

(*r*) *Arsenic(III) and antimony(III) and* (*V*). As(III) and Sb(III) are weakly adsorbed ($D_v \leqslant 1$) in the region, 1.0 to 12 M HBr. Sb(V), however, is strongly adsorbed ($D_v > 100$) from 9 to 12 M HBr solutions, presumably as negatively charged

$SbBr_6^-$. Hence, the oxidation states, Sb(III) and Sb(V), may readily be separated from each other by cation exchange in 9 to 12 M HBr solutions. In a typical experiment, a small sample containing tracer Sb(III) and Sb(V) in 9 M HBr was added to a 0.28 cm² × 3 cm column of Dowex 50-X4 which had been pretreated with 9 M HBr. On elution with 9 M HBr, Sb(III) appeared in a sharp band in the first c.v. of effluent while Sb(V) was retained. Removal of Sb(V) was effected with 9 M HBr containing *ca.* 0.05 M KI; this medium effectively reduces the adsorbed Sb(V) species to weakly adsorbed Sb(III).

(s) *Lead(II) and bismuth(III)*. These elements are adsorbable from dilute HBr solutions. Adsorbabilities decrease rapidly with increasing M HBr and become negligible ($D_v < 1$) above *ca.* 1 and 0.25 M HBr for Pb(II) and Bi(III), respectively. The differences in adsorbabilities of Pb(II) and Bi(III) in dilute HBr solutions are sufficiently large for convenient column separation of these elements from each other as illustrated earlier by FRITZ AND GARRALDA[7]. Numerous separations of Pb(II) and Bi(III) from elements which are adsorbed from high M HBr solutions may also be carried out, as illustrated in Fig. 25 by the separation of Pb(II) and Bi(III) from Po(IV).

Separations of Pb(II) from a number of elements more strongly adsorbed than Pb(II) have also been described by FRITZ AND GREEN[23]. These authors recommend the separations be carried out at elevated temperature (*ca.* 60°) to increase solubility of $PbBr_2$.

(t) *Uranium(IV) and (VI)* (*Figs. 12, 26, 27 and 28*). In HBr solutions, U(IV), at tracer concentrations, is readily oxidized to U(VI) by air. To circumvent this difficulty, D_v for U(IV) was measured by adding *ca.* 0.05 M U(IV) solutions to small columns and observing the rate at which the unoxidized U(IV) band (green) moved down the column during elution with appropriate HBr solutions. U(IV) is strongly adsorbed from dilute HBr solutions; adsorbability decreases sharply to a minimum $D_v = ca.$ 10 near 4.5 M HBr and then increases to D_v *ca.* 10^2 in 9 M HBr.
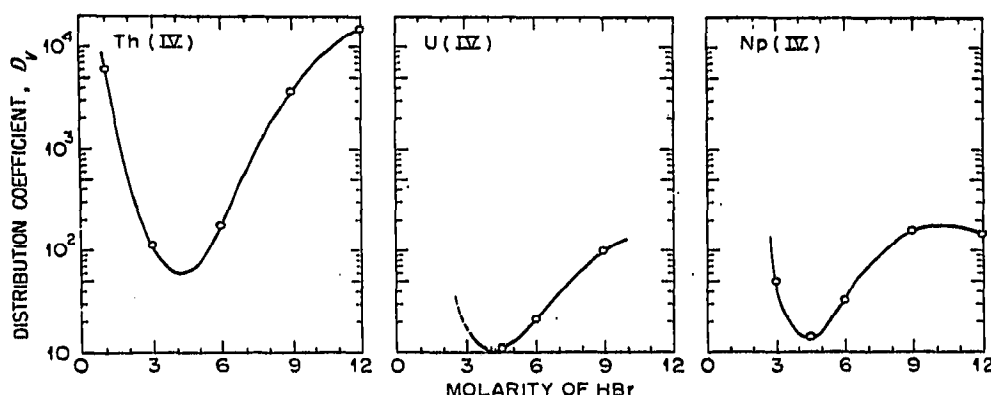
Fig. 26. Adsorption of Th(IV), U(IV) and Np(IV) from HBr solutions (Dowex 50-X4, 25°).

U(VI) is less strongly adsorbed than U(IV) from dilute and concentrated HBr solutions (see Fig. 12); adsorbability decreases to a minimum $D_v = 2.3$ near 8 M HBr, then slightly increases to $D_v = 2.6$ in 12 M HBr.

The marked differences in adsorbability between U(IV) and U(VI) in strong HBr solutions permits separation of these oxidation states from each other as illustrated
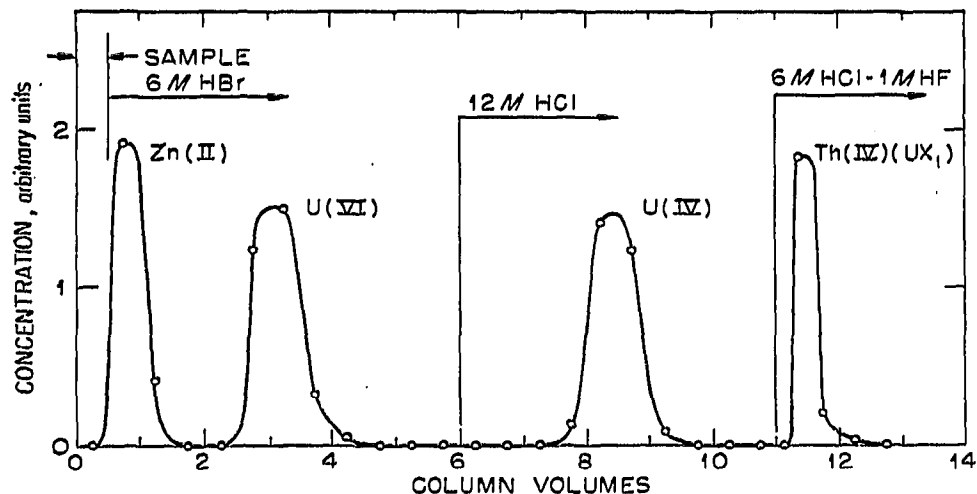
Fig. 27. Separation of Zn(II), U(VI), U(IV) and Th(IV) by cation exchange (Dowex 50-X4, 0.28 cm² × 4 cm column, 25°).

in Fig. 27. This separation also illustrates that the adsorbability of U(VI) at high M HBr, though low, is sufficient to permit separation of U(VI) from nonadsorbable elements, in this example, Zn(II). A 0.5 ml sample containing 0.05 M Zn(II), 0.05 M U(IV), and 0.05 M U(VI) in 6 M HBr was added to a 0.28 cm² × 4 cm column of Dowex 50-X4 which had been pretreated with 6 M HBr. On elution with 6 M HBr, Zn(II) and U(VI) appeared in separate bands with peak concentrations near 0.8 and 3.1 c.v., respectively. U(IV) was eluted with 12 M HCl, in which medium U(IV) is relatively weakly adsorbed[10]. Th(IV), present in the sample as UX₁ from the decay of natural uranium, was eluted with 6 M HCl-1 M HF.

(*u*) *Neptunium(IV), (V), and (VI)* (*Figs. 26, 28, and 29*). The adsorption function of Np(IV) resembles that of U(IV) (Fig. 26); adsorbability decreases to a minimum $D_v = ca.$ 15 near 4.5 M HBr, increases to a maximum $D_v = 160$ near 9 M HBr and then slightly decreases with increasing M HBr.

Np(IV) in high M HBr solutions may be separated from more weakly adsorbed
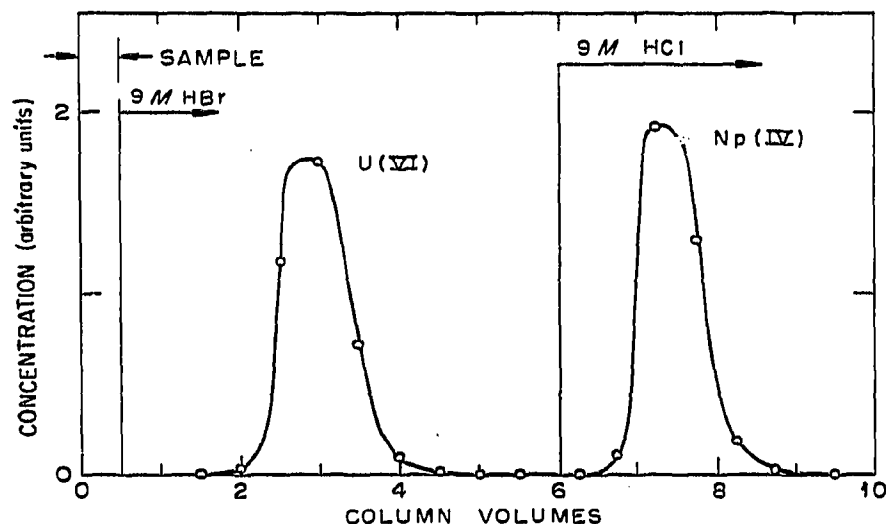

Fig. 28. Separation of U(VI) and Np(IV) by cation exchange (Dowex 50-X4, 0.2 cm² × 2 cm column, 25°).

elements, *e.g.*, U(VI) as illustrated in Fig. 28. A 0.2 ml sample containing 0.1 M U(VI) and tracer Np(IV) in 9 M HBr was added to a 0.2 cm² × 2 cm column of Dowex 50-X4 which had been pretreated with 9 M HBr. On elution with this same solution, U(VI) was removed in a sharp band with peak concentration near 3 c.v.; Np(IV) was removed with 9 M HCl, a medium in which its adsorbability is low[10].

Attempts were made to establish the adsorption behavior of the higher oxidation states of neptunium, Np(V) and Np(VI), both of which are expected to be much more weakly adsorbed than Np(IV) from high M HBr solutions by analogy with U(VI) and the behavior of Np(V) and Np(VI) in concentrated HCl solutions[10]. A small sample of Np(IV) tracer in 9 M HBr was treated with a few drops of liquid Br_2 as oxidizing agent and warmed several minutes. The sample was added to a small column of Dowex 50-X4 which had been pretreated with 9 M HBr–Br_2 solution. The column was then eluted with this same solvent. No Np activity appeared in the first 10 c.v. of effluent, suggesting that neptunium adsorbed on the column as Np(IV). Apparently, Br_2 is not strong enough an oxidizing agent to oxidize and hold neptunium in the (V) or (VI) states in the presence of the resin.

(v) Plutonium (III), (IV), and (VI) (Fig. 29). The predominant oxidation state of plutonium in concentrated HBr solutions presumably is Pu(III)[24], particularly if the solutions are heated to drive off bromine which may form from such oxidizing agents as air, HNO_3, etc. A stock solution of Pu(III) in 9 M HBr was prepared from a solution of Pu(IV) (²³⁸Pu tracer) in HNO_3. Excess 9 M HBr was added and the solution warmed to decompose HNO_3 and to drive out bromine. The solution was evaporated to a small volume (*ca.* 0.1 ml) and taken up in 9 M HBr; aliquots of this solution were used in preparing Pu(III) solutions for column experiments.

Adsorption measurements were carried out with *ca.* 3 to 12 M HBr solutions; adsorbability of Pu(III) decreases with increasing M HBr to a minimum $D_v = 3$ near 6 M HBr, then increases to $D_v = 15$ near 12 M HBr. The adsorption function of Pu(III) thus resembles that of Am(III) (Fig. 7).

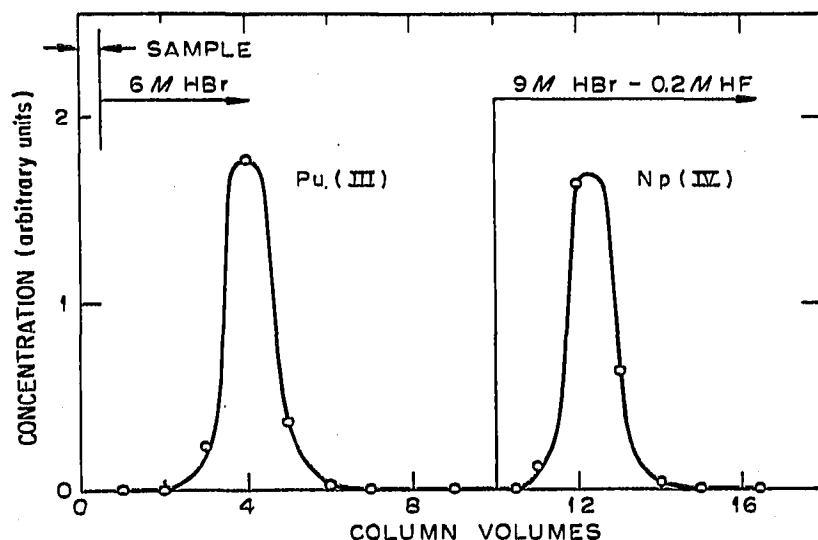Adsorbabilities of Pu(IV) and Pu(VI) in HBr solutions were not determined

Fig. 29. Separation of Pu(III) and Np(IV) by cation exchange (Dowex 50-X4, 0.28 cm² × 3 cm column, 60°).

because of difficulties in maintaining the elements in these oxidation states at high M HBr. Presumably the adsorption function of Pu(IV) resembles that of Np(IV) while the adsorption function of Pu(VI) resembles that of U(VI).

Since Pu(III) forms readily in concentrated HBr solutions and is weakly adsorbed from moderately concentrated (*e.g.*, 6 M HBr) solutions, its separation from Np(IV) is simple as illustrated in Fig. 29. For this separation, small aliquots of tracer Np(V) and Pu(IV) ([237]Np and [238]Pu) initially in HNO₃, were fumed to a small volume with excess 9 M HBr. This treatment presumably reduces Np(V) to Np(IV) and Pu(IV) to Pu(III). The residue was taken up in *ca.* 0.3 ml of 6 M HBr and added to a 0.28 cm² × 3 cm column of Dowex 50-X4 (60°) which had been pretreated with 6 M HBr. On elution with 6 M HBr, Pu(III) appeared in the effluent with peak concentration near 4 c.v. while Np(IV) was retained. Np(IV) was eluted in a sharp band with 9 M HBr–0.2 M HF solution; its rapid removal presumably results from the formation of weakly adsorbed Np(IV) fluoride complexes in this medium.

(*w*) *Other elements (nonmetals).* Adsorbability measurements were carried out with a number of nonmetallic elements as their common acids: H_3BO_3, HF, HCl, $HClO_4$, H_2SO_4, and H_3PO_4. Negligible or only slight adsorbability was found for *ca.* 0.1 M solutions of these acids in 1 to 12 M HBr.

2. Comparison of adsorbabilities of elements in HCl, HBr, and HClO₄ solutions

While a detailed comparison of the adsorption functions of the elements in HBr solutions with those published earlier[2] for the same resin in HCl and $HClO_4$ solutions is beyond the scope of this paper, some discussion of the relative adsorbabilities of elements in these three acids seems in order.

In the region of low HCl, HBr, and $HClO_4$ concentration (up to about 2 M) values of D_v for elements which are uncomplexed or weakly complexed by chloride or bromide (alkali metals, alkaline earths, etc.) are not markedly different in the three acids at a given acid concentration. The differences which occur presumably result from minor differences in the activity coefficients of the exchanging species. On the other hand, elements which are significantly complexed by chloride and bromide, *e.g.* Pb(II), Bi(III), Hg(II), Cd(II) show markedly lower adsorbabilities in HCl and HBr than in $HClO_4$ solutions at low acid concentrations. The chloride and bromide complexes of these elements presumably are relatively weakly adsorbed by the resin. However, low adsorbability from HCl or HBr solutions at low or moderate ionic strength does not preclude the possibility of strong adsorption of some elements as halide complexes (usually MX_4^-) at very high acid concentrations. For example, at very high acid concentrations, Fe(III) and Ga(III) are more strongly adsorbed from HCl and HBr solutions than from $HClO_4$ solutions.

In concentrated HCl, HBr, and $HClO_4$ solutions, the elements exhibit great diversity of adsorption behavior, particularly in the region 6 to 12 M. To illustrate, values of D_v for the elements in 9 M HCl, 9 M HBr, and 9 M HClO₄ solutions are compared in Table I. The data refer to the same Dowex 50-X4 resin. Values of D_v for 9 M HBr are from data obtained in this study; those for 9 M HCl and 9 M HClO₄ were taken for the most part from the earlier publication[2]. The value of D_v for Li⁺ in 9 M HClO₄ is a recent measurement carried out with a longer column than used earlier[2] in order to improve precision of the measurement; those for Ac(III) and Fr⁺ are from a recent paper in this series[8].

Table 1.

Distribution Coefficients of Elements in 9 M HCl, 9 M HBr, and 9 M HClO$_4$ (Dowex 50-X4)

Element	Distribution Coefficient, D_v			Element	Distribution Coefficient, D_v		
	9 M HCl	9 M HBr	9 M HClO$_4$		9 M HCl	9 M HBr	9 M HClO$_4$
Ac(III)	8.5	7.8×10^1	1×10^4	Os(IV)	<1	<1	
Ag(I)	<1	<1	2.4				
Al(III)	0.6	0.3	3.8	P(H$_3$PO$_4$)	<1	<1	1
Am(III)	1.2	5.9	2.0×10^3	Pa(V)	<1	$>1 \times 10^1$	$>1 \times 10^3$
As(III)	<1	<1	0.4	Pb(II)	<0.5	<1	1.9×10^1
As(V)	<1		1.4	Pd(II)	<1	<1	
Au(III)	1.2×10^2	6.1×10^1		Po(IV)	<1	1.2×10^1	<1
				Pt(IV)	<1	<1	
B(H$_3$BO$_3$)	<1	<1	1	Pu(III)		6	
Ba(II)	4.5	1.1×10^1	4.9	Pu(VI)	<1		$>1 \times 10^2$
Be(II)	0.3	<1	1.3				
Bi(III)	<1	<1	8.6×10^2	R.E.(III)			
Br(Br$^-$)	<1		<1	La(III)	4.5	1.7×10^1	3.3×10^3
				Eu(III)		7.2	2.0×10^3
Ca(II)	3.2	6.4	1.4×10^2	Yb(III)	1.0		1.3×10^2
Cd(II)	<1	<1	1.7×10^1	Lu(III)	0.8	1.3	8.7×10^1
Cl(Cl$^-$)	<1	<1	<1	Ra(II)	2.5	5.6	2.0
Cl(ClO$_4^-$)		<1		Rb(I)	<1	<1	<0.5
Cm(III)	1	6.4	$>1 \times 10^3$	Re(VII)	<0.8	1.3	<1
Co(II)	0.3	<1	1.5	Rh(III)	<1	<1	
Cr(III)	<1	<1	2.0	Ru(IV)	<1	<1	
Cr(VI)	<1		$>1.0 \times 10^2$				
Cs(I)	<1	<1	0.6	S(HSO$_4^-$)	<1	<1	1
Cu(II)	0.4	<1	1.2	Sb(III)	<1	<1	1
				Sb(V)	2×10^3	$>1 \times 10^2$	
F(HF)	<1	<1	<1	Sc(III)	1.7×10^1	3.3×10^2	7.2×10^5
Fe(III)	3×10^2	2.5×10^3	1.8×10^1	Se(IV)	<1	1.2	0.7
Fr(I)	<1	<1	<1	Sn(IV)	<1	1.7	
				Sr(II)	3.5	8.7	2.9×10^1
Ga(III)	3.3×10^2	1×10^3	1.3×10^1				
				Ta(V)	1	$>1 \times 10^1$	$>1 \times 10^3$
Hf(IV)	<1	5.4	9.6×10^1	Tc(VII)	<0.5	<2	<1
Hg(II)	<1	<1	7	Te(IV)	<1	4.0	2.8
				Th(IV)	2.8×10^1	3.6×10^3	$>1 \times 10^7$
I(I$^-$)	<1	<1	<1	Ti(IV)	1	3.0	1.9×10^3
In(III)	<1	8.0×10^1	9.5	Tl(III)	5.3	6.0×10^2	1
Ir(III)	<1	<1					
Ir(IV)	<1	<1		U(IV)		$>1 \times 10^2$	
				U(VI)	0.5	2.3	3.8×10^3
K(I)	<1	<1	0.3				
				V(IV)	<1	<1	2.1×10^1
Li(I)	<1	1.0	1.8	V(V)	2		$>1 \times 10^2$
Mg(II)	0.3	<1	1.9	W(VI)	<1	<1	$>5 \times 10^2$
Mn(II)	0.4	<1	1.9×10^1				
Mo(VI)	<1	4.5	8.7×10^2	Y(III)	1.6	3.5	5.8×10^2
N(NO$_3^-$)	<1		1.5				
Na(I)	<1	<1	<0.5	Zn(II)	<1	<1	1.8
Nb(V)	1.6	>3	$>1 \times 10^3$	Zr(IV)	1	8	2.1×10^2
Ni(II)	<1	<1	1.0				
Np(IV)		1.6×10^2					
Np(VI)	<1		$>1.0 \times 10^2$				

Fig. 30. Adsorption of the elements from HBr solutions by a cation exchange resin.

The data of Table I show that many more elements are moderately strongly or strongly adsorbed from 9 M $HClO_4$ solutions than from 9 M HBr or 9 M HCl solutions and, in general, that a given element, if adsorbed at all, is usually more strongly adsorbed from 9 M HBr solutions than from 9 M HCl solutions. Thus, as mentioned in Section 1-b, adsorption order of an element usually reflects the order of the activity coefficients ($\gamma_{\pm}$) of the acids (and, presumably, of the salts) at high concentrations i.e., $\gamma_{\pm HClO_4} > \gamma_{\pm HBr} > \gamma_{\pm HCl}$, or conversely, the inverse order of the water activity (a_{H_2O}) in the acids.

Adsorbabilities of some elements, particularly those of high valence, often differ widely in the three acids. Thus for Th(IV), D_v is $> 10^7$, $3.6 \cdot 10^3$, and 28 in 9 M $HClO_4$, 9 M HBr and 9 M HCl; for Sc(III), the corresponding values are $7.2 \cdot 10^5$, $3.3 \cdot 10^2$, and 17, respectively. For many other elements, the differences are smaller but still appreciable; for example, for Ca(II), D_v is $1.4 \cdot 10^2$, 6.4, and 3.2 in 9 M HCl, 9 M HBr, and 9 M HCl, respectively, and corresponding values of D_v for U(VI) are $3.8 \cdot 10^3$, 2.3, and 0.5, respectively. Elements of unit positive charge show low adsorbabilities and small differences in adsorbability. Thus for Li+, D_v is 1.8 in 9 M $HClO_4$, 1 in 9 M HBr, and < 1 in 9 M HCl.

As pointed our earlier[2], the reasons for the high selectivity of Dowex 50 for some elements in concentrated acid solutions are not understood. The high selectivities of some elements of high valence type e.g. Th(IV), Sc(III), R.E.(III), U(VI) especially in high M $HClO_4$ solutions may well mean that these elements form strong association complexes with the sulphonate groups on the resin network.

Pronounced departures from the usual adsorption order, i.e., $HClO_4 >$ HBr > HCl, occur for elements which adsorb from HCl and HBr solutions presumably as negative halide complexes. For example, In(III) and Tl(III) are more strongly adsorbed from HBr solutions than from HCl and $HClO_4$ solutions, as are Ga(III), Fe(III), Te(IV), and Po(IV). Au(III), however, is more strongly adsorbed from HCl than HBr solutions.

Many of the elements which are adsorbed from HCl and HBr solutions apparently as negative species also are readily extracted from the HCl and HBr solutions into ethers[25-27]. However, as discussed earlier[15], the relationship between cation exchange adsorbability of these elements and their ether extraction behavior is not understood.

CONCLUSIONS

The adsorption data for the elements in HBr solutions are summarized in Fig. 30, a "periodic table" arrangement of plots of log D_v vs. molarity of HBr. The adsorption functions are comparable since they refer to the same batch of Dowex 50-X4 resin and were determined under conditions of low loading of the resin by the elements, i.e., nearly always less than 1 % of capacity. The principle features of the adsorption functions may be summarized as follows:

(a) Many elements which form very stable bromide complexes, e.g., platinum elements, are not significantly adsorbed from ca. 0.5 to 12 M HBr; presumably they also are nonadsorbable at HBr concentrations lower than 0.5 M provided adsorbable hydrolytic species are not formed. Similar low adsorbability is shown by most of the nonmetallic elements as their common acids e.g. HF, H_2SO_4, H_3PO_4, $HClO_4$.

(b) Several elements, Mg(II), V(IV), Al(III), Zn(II), etc., are strongly adsorbed

from very dilute HBr solutions. Adsorbability decreases with increasing HBr concentration and becomes negligible in dilute to moderately concentrated HBr solutions. For some of these elements, particularly those which form stable and moderately stable but weakly adsorbed bromide complexes, Cd(II), Hg(II), Pb(II) etc., adsorption decreases very steeply with increasing M HBr and becomes negligible at relatively low HBr concentrations.

(c) Most elements in HBr solutions show adsorption minima. Many of these elements, Ca(II), R.E.(III), Th(IV), etc., presumably are adsorbed at all HBr concentrations as cationic species. Others, however, e.g., Fe(III), Ga(III), In(III), apparently are adsorbed as cationic species at low HBr concentrations and as anionic species at high HBr concentrations.

(d) Some elements, Au(III), Tl(III), Po(IV), etc., which presumably exist in HBr solutions as negatively charged bromide complexes over a very wide range of HBr concentration, show the expected low adsorbability in dilute HBr solutions, but are significantly adsorbed from strong HBr solutions apparently as negative complexes.

Numerous column separations may be designed from the data given in Fig. 30, some of which were illustrated in this paper. The wide differences in adsorption behavior in dilute HBr solutions permit many separations in which elements are adsorbed from dilute HBr (or other acid solutions) and sequential elution is accomplished with HBr solutions of progressively increasing HBr concentration. Conversely, many elements may be adsorbed from concentrated HBr solutions and sequential elution achieved with solutions of decreasing HBr concentration or with other acids, or acid mixtures, e.g., HCl, HNO_3, HBr–HF, and HCl–HF solutions.

Concentrated HBr solutions appear particularly useful as separation media since they are excellent solvents for many materials. Thus in the classical NOYES AND BRAY scheme of analysis[5], concentrated HBr–Br_2 solutions are used extensively as solvents. Since hydrobromic acid is usually purchased as the constant boiling mixture (ca. 9 M HBr), acid of this composition appears especially attractive for cation exchange separations; it should be particularly useful for major group and subgroup separations.

SUMMARY

Results of a systematic study of the cation exchange behavior of elements in HBr solutions are given for a Dowex 50 resin. Many elements show adsorption minima at moderate HBr concentrations followed by a rapid increase in adsorbability at high HBr concentrations. Marked differences in adsorbabilities of the elements occur, particularly in dilute and concentrated HBr solutions. Implications of the data for separations are discussed and typical separations illustrated.

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