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ION-EXCHANGE PROCEDURES

X*. CATION EXCHANGE IN CONCENTRATED $HClO_4$–HCl SOLUTIONS

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SUMMARY

The cation-exchange behavior of a number of elements in concentrated $HClO_4$–HCl mixtures has been studied with a Dowex 50 resin. Adsorption data as a function of acid composition and application of the data to column separations are given. Activity coefficients of HCl and $HClO_4$ in the resin phase have been determined for two- and three-component aqueous systems. Some implications of the results for determination of complex constants of species in the aqueous phase are discussed.

INTRODUCTION

In a previous paper[2], cation-exchange adsorption functions of most of the elements in HCl and $HClO_4$ solutions were given for a Dowex 50 resin over a wide range of acid concentrations. Adsorbabilities of many elements go through minima at moderate acid concentrations (4–6 *M*) and then increase rapidly with increasing HCl or $HClO_4$ concentration.

The strong and sometimes unique adsorption at high HCl or $HClO_4$ concentration can be utilized for separations. Since many more elements are adsorbed from concentrated $HClO_4$ solutions than from concentrated HCl, $HClO_4$ might appear far more useful than HCl for resolving mixtures of elements into "adsorbed" and "weakly adsorbed" or "non-adsorbed" groups. However, use of $HClO_4$ alone is sometimes restricted. Several elements, *e.g.*, the platinum metals, Ta(V), W(VI) and Sn(IV), precipitate from $HClO_4$ solutions or form troublesome hydrolytic species unless a complexing agent such as HCl or HF is added. We have examined concentrated (9 *M*) $HClO_4$–HCl mixtures as media for cation-exchange separations; this paper presents the results.

Adsorption functions were measured in 9 *M* $HClO_4$–HCl mixtures over a wide range of compositions with emphasis on those elements that are strongly adsorbed from concentrated HCl or $HClO_4$ solution; typical column separations based on the data are also described.

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[*] For Part IX, see ref. 1.

EXPERIMENTAL

Adsorbabilities were determined with the same batch of cation-exchange resin (Dowex 50-X4; 270–325 mesh in water) used in previous studies[2]. The resin had a capacity of 5.12 equiv. per kg of dry resin.

The experimental procedures and analytical methods (usually radiometric) for determining distribution coefficients were described earlier[2]. Since tracer, or otherwise low, concentrations of the elements were used, loading of the resin was always low, *i.e.*, less than 1% of capacity. Adsorbability is usually expressed as volume distribution coefficient, D_v, (amount adsorbed per liter of resin bed/amount per liter of solution) because of the close relationship of D_v to elution-band positions: $(\text{c.v.})_{\text{max.}} = D_v + i$, where $(\text{c.v.})_{\text{max.}}$ is the number of (geometric) column volumes at which the elution-band peak is observed and $i \approx 0.4$ is the fractional interstitial volume.

When adsorbability was low, the band-elution method was used to measure D_v. When adsorbability was high ($D_v > \approx 10$), batch-equilibration methods were used; values of D_v were computed from the weight-distribution coefficients (D) (amount adsorbed per kg of dry resin/amount per liter of solution) and the bed densities (ϱ) by the relationship, $D_v = D\varrho$. The value of $1/\varrho$ (liters of bed per kg of dry resin) was 2.08 in 9 M $HClO_4$ and 2.22 in 9 M HCl; $1/\varrho$ was assumed to vary linearly with F_{HCl}, the fraction of HCl in the mixtures.

Small columns, usually 0.6 cm in diameter, were prepared from polypropylene or from Fluorothene tubing. The tubing was heated and drawn out to a tip at one end, and a porous Teflon plug was inserted to retain the resin. Bed heights were usually 2 to 6 cm for determining distribution coefficients and for separations. Temperature was controlled by placing the columns into jackets through which water at controlled temperature was pumped. To improve the elution kinetics, most separations were carried out at elevated temperature and with a fine mesh of Dowex 50-X4 (20–30 μm diameter in water).

The composition of the resin in equilibrium with various acid solutions was established by methods described earlier[3]. Resin samples (0.5–1 g) were treated in small columns with appropriate acid solutions. After equilibration, the columns were centrifuged to remove most of the interstitial solution, weighed and washed with distilled water to remove the imbibed and adhering acid; the concentration of acid in the wash was determined by titration with standard base. When both HCl and $HClO_4$ were present, the HCl concentration was separately determined by titrating a portion of the effluent with standardized $AgNO_3$ solution. The $HClO_4$ concentration was then computed from the difference between the total acid and the chloride concentrations. From the weighing and titration data, the amounts of HCl, $HClO_4$ and water per kg of dry resin were computed after correction for the amount of solution adhering to the resin after centrifuging; the amount of solution so held was assumed to be 0.033 liters per liter of bed, a value found earlier[3] with fine-mesh glass beads under similar centrifugation conditions.

RESULTS AND DISCUSSION

Adsorption of $HClO_4$ and HCl; activity coefficients in the resin

To characterize the resin, acid invasion in 1–15.5 m $HClO_4$ and 1–16 m HCl was measured (m is moles/kg of water). The results, summarized in Table I, are in agreement with similar data of Choppin and Dinnius[4] for a different batch of Dowex 50-X4 resin. The concentration of $HClO_4$ or HCl in the resin increases rapidly with increasing m_{HClO_4} or m_{HCl}, while the water content of the resin decreases from 1.866 kg H_2O/kg dry resin in water to 0.411 kg H_2O/kg resin in 14.5 m $HClO_4$ and to 0.551 kg H_2O/kg resin in 16 m HCl. As noted earlier[2], the volumes of beds prepared from this resin also decrease substantially with increasing m_{HClO_4} or m_{HCl}.

TABLE I

ACID INVASION AND ACTIVITY COEFFICIENTS OF $HClO_4$ AND HCl IN DOWEX 50-X4 RESIN AT 25°

For $HClO_4$

m_{HClO_4}	$m_{HClO_4\,(r)}$	$m_{H\,(r)}$	Water content (kg of H_2O/kg of resin)	Γ_{HClO_4}	$\gamma_{\pm HClO_4\,(r)}$
0	0	2.74	1.866		
1.05	0.23	3.57	1.535	1.16	0.96
3.44	1.40	5.83	1.155	1.20	2.04
6.40	3.33	9.29	0.858	1.15	6.56
8.01	4.48	11.42	0.737	1.12	13.3
12.2	7.93	18.3	0.494	1.02	90
14.5	12.38	22.9	0.411	0.93	233

For HCl

m_{HCl}	$m_{HCl\,(r)}$	$m_{H\,(r)}$	Water content (kg of H_2O/kg of resin)	Γ_{HCl}	$\gamma_{\pm HCl\,(r)}$
1.03	0.21	3.51	1.55	1.19	0.96
2.10	0.66	4.48	1.34	1.22	1.23
4.37	1.93	6.68	1.08	1.22	2.35
6.90	3.65	9.45	0.884	1.18	4.99
11.21	7.03	14.7	0.670	1.11	16.0
14.5	9.65	18.4	0.579	1.08	33.5
16.0	10.74	20.1	0.551	1.09	44.5

The activity coefficients, $\gamma_{\pm(r)}$ of the acids in the resin were computed from the invasion data. By choosing the same standard states for the electrolytes in the resin and aqueous phases and expressing concentrations in moles per kg of water (m) in the phases, one can write the following relationships for the activity of HCl and $HClO_4$:

$$a_{HCl} = m_H m_{Cl}\, \gamma^2_{\pm HCl} = m_{H(r)} m_{Cl(r)}\, \gamma^2_{\pm HCl(r)} \tag{1}$$

and

$$a_{HClO_4} = m_H m_{ClO_4}\, \gamma^2_{\pm HClO_4} = m_{H(r)} m_{ClO_4(r)}\, \gamma^2_{\pm HClO_4(r)} \tag{2}$$

where the subscript (r) designates the resin phase. The invasion data, together with reported activity coefficients of $HClO_4$ and HCl in aqueous solutions[5,6], permit computation of $\gamma_{\pm HClO_4(r)}$ and $\gamma_{\pm HCl(r)}$. Although the activity coefficients of $HClO_4$ and

HCl in the resin increase rapidly with acid concentration, the ratios $\Gamma_{HCl} = \gamma_{\pm HCl(r)}/\gamma_{\pm HCl}$ and $\Gamma_{HClO_4} = \gamma_{\pm HClO_4(r)}/\gamma_{\pm HClO_4}$ are similar in the two media and are near unity over the whole concentration range studied.

With current information on the invasion of HCl and $HClO_4$, values of K/Γ may be computed for the adsorption equilibria of the various elements in the Periodic Table published earlier[2]. The term K/Γ is defined by the conventional ion-exchange equation:

$$K = \frac{m_{M(r)} m_H^{\nu}}{m_M m_{H(r)}^{\nu}} \frac{\gamma_{M(r)} \gamma_H^{\nu}}{\gamma_M \gamma_{H(r)}^{\nu}} = D'_M \frac{m_H^{\nu}}{m_{H(r)}^{\nu}} \Gamma \tag{3}$$

where ν is the charge on the adsorbed ion M and $\Gamma = (\gamma_{\pm MX_{\nu}(r)}/\gamma_{\pm MX_{\nu}})^{\nu+1} (\gamma_{\pm HX}/\gamma_{\pm HX(r)})^{2\nu}$ and D'_M is the distribution coefficient of M expressed as moles per kg of water on the resin/moles per kg of water in the aqueous phase.

From our earlier data[2], we have computed values of K/Γ for four representative elements [Cs(I), Ca(II), La(III) and Th(IV)] and show these in Fig. 1. Instead of plotting these values against molality of the electrolytes, we elected to plot $m\Phi$, where Φ is the osmotic coefficient[6]. This variable is closely related to the activity of water, a_{H_2O}, in these solutions ($\log a_{H_2O} = -0.0156\, m\Phi$). We thought this variable might be a logical one for comparing properties of the elements in these different (concentrated) electrolyte solutions. Note that at a given value of $m\Phi$ the concentrations of m_{HCl} and m_{HClO_4} may differ considerably. Typical values for $m\Phi = 10$, 20 or 40 are $m_{HCl} = 5.6$, 8.7 or 14.6 and $m_{HClO_4} = 5.2$, 7.7 or 11.3, respectively.

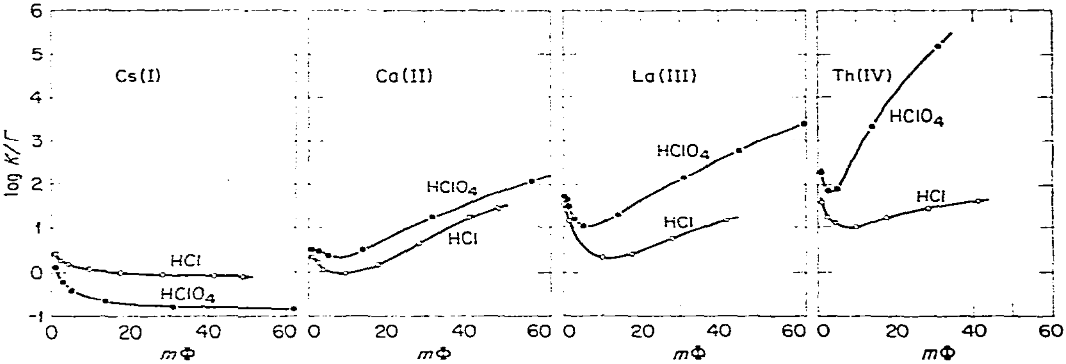

Fig. 1. Adsorption of Cs(I), Ca(II), La(III) and Th(IV) from $HClO_4$ and HCl solutions on Dowex 50-X4 resin at 25°.

Inspection of Fig. 1 shows that, at low ionic strength ($\mu < 0.1$), K/Γ for the metal ions in $HClO_4$ and HCl solutions approach each other (as expected); at moderate or high ionic strengths, significant divergences occur.

For Cs(I) in HCl and $HClO_4$ solutions, log K/Γ at first decreases with increasing $m\Phi$ (decreasing water activity) and then levels out at higher values of $m\Phi$. At a solution-phase ionic strength of 1 *m*, K/Γ for $HClO_4$ is larger by a factor of *ca.* 2 than the corresponding value for HCl solutions; at very high ionic strengths, the differences in K/Γ are even larger, but the curves for log K/Γ parallel each other.

For Ca(II) in $HClO_4$, log K/Γ decreases to a minimum near $m\Phi = 10$ and then increases almost linearly with increasing $m\Phi$. The corresponding function for Ca(II) in HCl parallels that for $HClO_4$, but, at a high $m\Phi$, K/Γ values are lower by a factor of *ca.* 4 in HCl solutions than in $HClO_4$ solutions of the same water activity.

For La(III) and Th(IV) in $HClO_4$, log K/Γ decreases with $m\Phi$ to a minimum and then increases rapidly with increasing $m\Phi$. In the region $m\Phi$ = *ca.* 20 to 40, where a_{H_2O} varies from *ca.* 0.6 to 0.3, the slope $d\log(K/\Gamma)/d(m\Phi)$ corresponds approximately to a sixth-power dependence on a_{H_2O} for Th(IV) and a third-power dependence on a_{H_2O} for La(III). At high ionic strength, K/Γ values for Th(IV) in HCl are markedly lower than the corresponding values for $HClO_4$ solutions, and the slope $[d\log(K/\Gamma)/d(m\Phi)]$ is relatively small.

It seems reasonable to ascribe the large difference in adsorbability of Th(IV) in $HClO_4$ and HCl solutions to extensive chloride complexing at high ionic strength. If we assume that in the absence of chloride complexing the curve of K/Γ in HCl would parallel the curve in $HClO_4$, one estimates that the fraction of Th(IV) uncomplexed in the most concentrated HCl solutions plotted in Fig. 1 ($m_{HCl} \approx 14$) is of the order of 10^{-3}. The divergence of the curves for La(III) is much less dramatic than that for Th(IV). Thus, the conclusion that La(III) is complexed by chloride ions, on the basis of these results, is much less certain than for Th(IV). Again, if we assume that the curves should be parallel in the absence of chloride complexing, one makes the (uncertain) estimate that at least 10% of the La(III) remains uncomplexed in the most concentrated HCl solutions plotted in Fig. 1.

Adsorption of $HClO_4$ and HCl from $HClO_4$–HCl mixtures

The acid mixtures were prepared from reagent-grade concentrated HCl and $HClO_4$. If these concentrated solutions are mixed, there is vigorous evolution of HCl gas. To establish the upper limits of compositions that can be prepared without producing excessive HCl vapor pressure, the activity of HCl in $HClO_4$–HCl mixtures was estimated. This, in turn, required estimation of the activity coefficient of HCl in the mixtures as a function of F_{HCl}, the fraction of HCl. The activity coefficients were computed from those of the two-component systems[6] on the assumption that the Brønsted theory holds[6], *i.e.*, that, at constant molality, log $\gamma_{\pm HCl}$ in the mixture is a linear function of F_{HCl} and at $F_{HCl} = 0$ is equal to 0.5 $\log(\gamma_{\pm HClO_4}/\gamma_{\pm HCl})$ of the two-component systems of the same ionic strength. The results for $HClO_4$–HCl mixtures at 25° are shown in Fig. 2, semi-logarithmic plots of activity a_{HCl} *vs.* F_{HCl} computed for various total molarities, M (moles per liter).

As shown in Fig. 2, a_{HCl} rises rapidly with increasing F_{HCl} to maxima near $F_{HCl} = 0.2$ and then decreases with further increase in F_{HCl}. For comparison, the activity of nearly saturated HCl (12 M) is shown as a dashed line in the figure; when a_{HCl} for a particular mixture lies below this line no troublesome evolution of HCl should occur, whereas if it lies above the line, the mixture should be unstable at normal pressures. Mixtures of $HClO_4$–HCl of concentration 9.5 M or less thus should be reasonable stable at all values of F_{HCl}. At acid concentrations somewhat greater than 9.5 M, the solutions are probably unstable with respect to HCl gas evolution in the region near F_{HCl} = *ca.* 0.2. At high acid concentrations (10.5–12 M) the solutions are unstable except at very low or very high values of F_{HCl}.

Adsorption of $HClO_4$ and HCl by the resin in $HClO_4$–HCl mixtures of constant

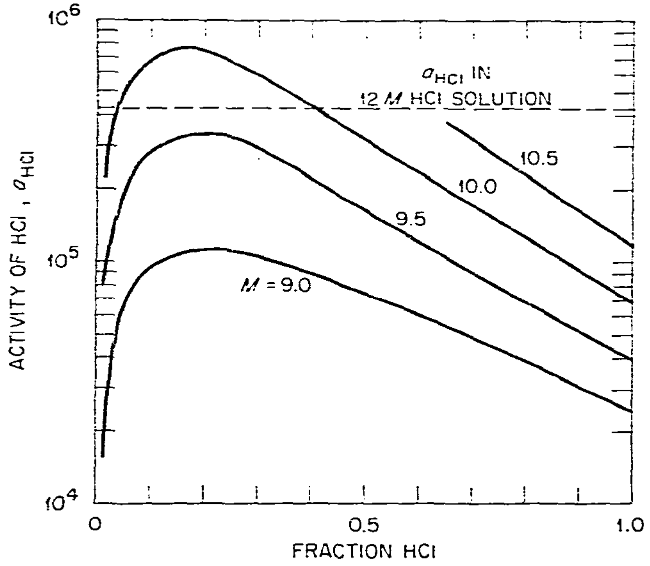

Fig. 2. Activity of HCl in $HClO_4$–HCl mixtures at constant total molarity at 25°.

ionic strength (14.5 m) was measured with solutions prepared by mixing 14.5 m $HClO_4$ and 14.5 m HCl. The results are summarized in Table II. Preferential adsorption of one acid over the other does not occur to any significant extent. The uptake of HCl by the resin, $m_{HCl(r)}$, increases approximately linearly with F_{HCl} in the acid mixtures and is accompanied by an almost corresponding decrease in $m_{HClO_4(r)}$. The ratio of the activity coefficients of $HClO_4$ and HCl in the resin and solution phases (Γ_{HClO_4} and Γ_{HCl}, respectively) computed from the invasion data and equations 1 and 2 are near unity, as for the two-component (aqueous) systems. The activity coefficients of $HClO_4$ and HCl in the resin are also given in Table II; these values were computed by using estimated values of $\gamma_{\pm HCl}$ and $\gamma_{\pm HClO_4}$ for the acid mixtures. The latter were obtained, as described above, from the Brønsted relationship.

Adsorption functions in 9 M $HClO_4$–HCl mixtures (Fig. 3)

To evaluate concentrated $HClO_4$–HCl mixtures as separations media, D_v values of selected elements were measured for acid mixtures at constant total molarity (9 M).

TABLE II

ADSORPTION OF HCl AND $HClO_4$ FROM MIXTURES

The sum of $m_{HCl} + m_{HClO_4} = 14.5$; Dowex 50-X4 resin at 25°.

F_{HCl}	$m_{HCl\,(r)}$	$m_{HClO_4\,(r)}$	$m_{H\,(r)}$	$\frac{kg\ H_2O}{kg\ res}$	Γ_{HCl}	Γ_{HClO_4}	$\gamma_{\pm HCl\,(r)}$	$\gamma_{\pm HClO_4\,(r)}$
0.0	0.0	10.48	22.86	0.41	—	0.93	—	244
0.155	1.55	8.44	20.62	0.48	1.00	1.00	75.	220
0.289	2.83	7.05	20.19	0.50	1.03	1.02	68.6	196
0.531	5.25	4.83	19.50	0.54	1.04	1.02	52.8	150
0.766	7.37	2.57	18.63	0.58	1.07	1.02	42.8	117
1.00	9.65	0.0	18.44	0.58	1.08	—	33.5	—

This concentration for acid mixtures was chosen since it seemed the highest practical concentration usable. Aside from possible HCl gas evolution at higher concentrations, exchange rates also become increasingly unfavorable, particularly when F_{HClO_4} is large. At much lower acidities, of course, the differences between the two media are less dramatic, and distribution coefficients tend to be significantly lower. The adsorption studies reported here, and summarized in Fig. 3, primarily concern elements that are moderately or strongly adsorbed from 9 *M* $HClO_4$ or 9 *M* HCl solutions since preliminary measurements showed that those elements (such as the alkali metals and halides) which are weakly adsorbed ($D_v <$ *ca.* 2) from both 9 *M* $HClO_4$ and 9 *M* HCl also are weakly adsorbed from 9 *M* $HClO_4$–HCl mixtures.

Some general comments can be made concerning the characteristics of the adsorption functions:

The adsorbability of most elements decreases with increasing F_{HCl}; for several, *e.g.*, Bi(III), Cd(II) and U(VI), D_v decreases very rapidly with increasing F_{HCl} and becomes less than unity even at relatively low values of F_{HCl}. These rapid decreases in adsorbability almost surely result from formation of non-adsorbable or weakly adsorbed chloride complexes, probably negatively charged.

For several elements, *e.g.*, trivalent lanthanides, Ca(II) and Sr(II), D_v decreases gradually with increasing F_{HCl}; for these elements, log D_v varies almost linearly with F_{HCl}.

A few elements, known to be extensively complexed by chloride [*e.g.*, Fe(III), Ga(III), Au(III) and Sb(V)], show little change or increasing adsorbability with increasing F_{HCl}; presumably these elements are adsorbed by cation exchangers as negatively charged complexes[7].

Adsorption functions are described in more detail below, together with some applications of the data to column separations. For the latter, a solution composition of 8.5 *M* $HClO_4$–0.5 *M* HCl was particularly convenient, since a fairly large number of elements is strongly adsorbed from this medium and the HCl concentration, though low, is sufficiently high to complex strongly many of those elements [*e.g.*, platinum metals, Zr(IV), Sn(IV) and W(VI)] that normally hydrolyze in $HClO_4$.

Alkaline Earths (Figs. 4 and 5). Ca(II) and Sr(II) are moderately strongly adsorbed from 9 *M* $HClO_4$, where $D_v = 140$ and 30, respectively; Ba(II) is only slightly adsorbed ($D_v = 4.9$); Be(II), Mg(II) and Ra(II) are weakly adsorbed ($D_v < 2.5$). In 9 *M* HCl, Ca(II), Sr(II), Ba(II) and Ra(II) are only slightly adsorbed ($D_v = 2.5$–4.5), while Be(II) and Mg(II) are negligibly adsorbed, ($D_v < 1$). In 9 *M* $HClO_4$–HCl mixtures, adsorption of the alkaline-earth elements decreases with increasing F_{HCl}, except for Ba(II) and Ra(II), which show little change in adsorbability. Plots of log D_v *vs.* F_{HCl} are approximately linear functions as shown in Fig. 4.

These functions may be used to devise separations of some of the alkaline-earth elements from each other by column techniques. Separation of Ca(II) from Mg(II) was reported earlier[8] and is particularly favorable at low or moderate F_{HCl} where Ca(II) is strongly adsorbed and Mg(II) weakly adsorbed. Similar results should be obtained with Be(II).

Sr(II) and Ba(II) may also be conveniently separated at low F_{HCl} as illustrated in Fig. 5. For this separation, a 0.5-ml aliquot containing a weakly adsorbed element (^{134}Cs), ^{133}Ba and ^{85}Sr in 8.5 *M* $HClO_4$–0.5 *M* HCl was added to a 0.25-cm^2 × 6-cm column of Dowex 50-X4 resin. The column was operated at 50° to

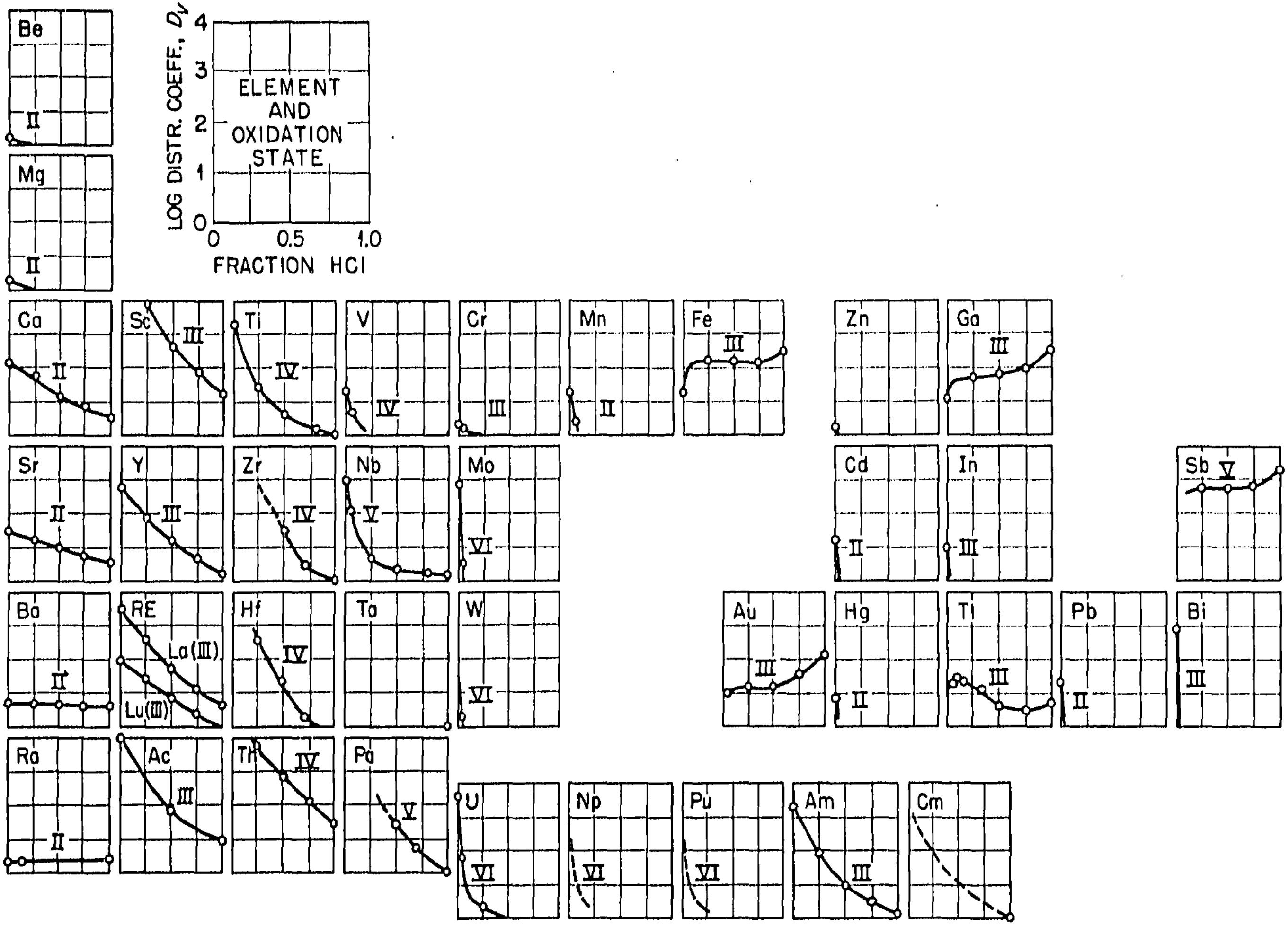

Fig. 3. Adsorption of elements from 9 *M* $HClO_4$–HCl mixtures by a cation-exchange resin.

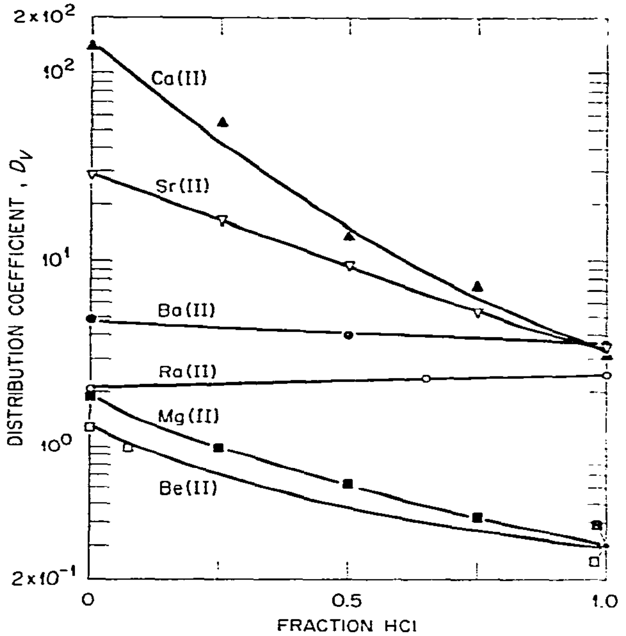

Fig. 4. Adsorption of alkaline-earth elements from 9 *M* $HClO_4$–HCl mixtures on Dowex 50-X4 resin at 25°.

improve the kinetics. On elution with the same acid mixture, Cs(I) and Ba(II) were removed in separate bands with peak concentrations near 1 and 4 (geometric) column volumes (c.v.) of effluent respectively, while Sr(II) remained adsorbed. Sr(II) was removed with *ca.* 4 c.v. of 5 *M* HCl, a medium in which its adsorbability is low.

Sc(III), Y(III) and trivalent lanthanides (Figs. 6 and 7). These elements are strongly adsorbed from 9 *M* $HClO_4$ ($D_v = 87$ to *ca.* 10^5), while in 9 *M* HCl adsorbabilities are considerably lower ($D_v = 0.8$ to 17). Adsorption functions

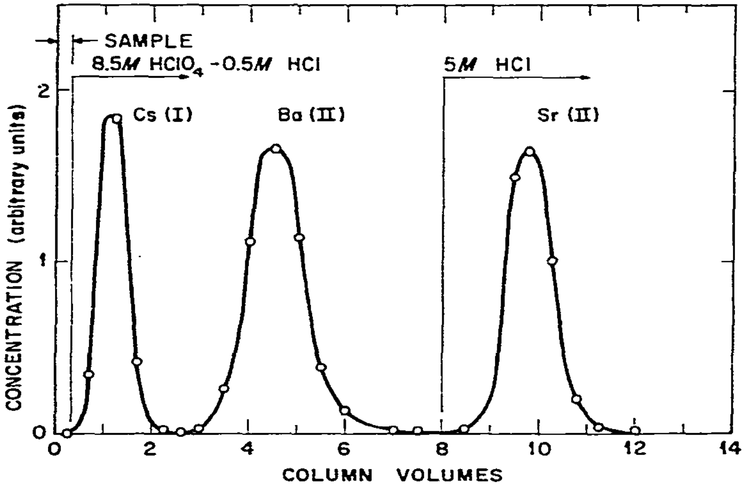

Fig. 5. Separation of Cs(I), Ba(II) and Sr(II) by cation exchange on Dowex 50-X4 resin at 50°.

of Sc(III), Y(III) and the lightest and heaviest lanthanides [La(III) and Lu(III)] in 9 *M* $HClO_4$–HCl mixtures are shown in Fig. 6, a semi-logarithmic plot of D_v *vs.* F_{HCl}. Adsorption functions of the other lanthanides may be presumed to lie between those for La(III) and Lu(III).

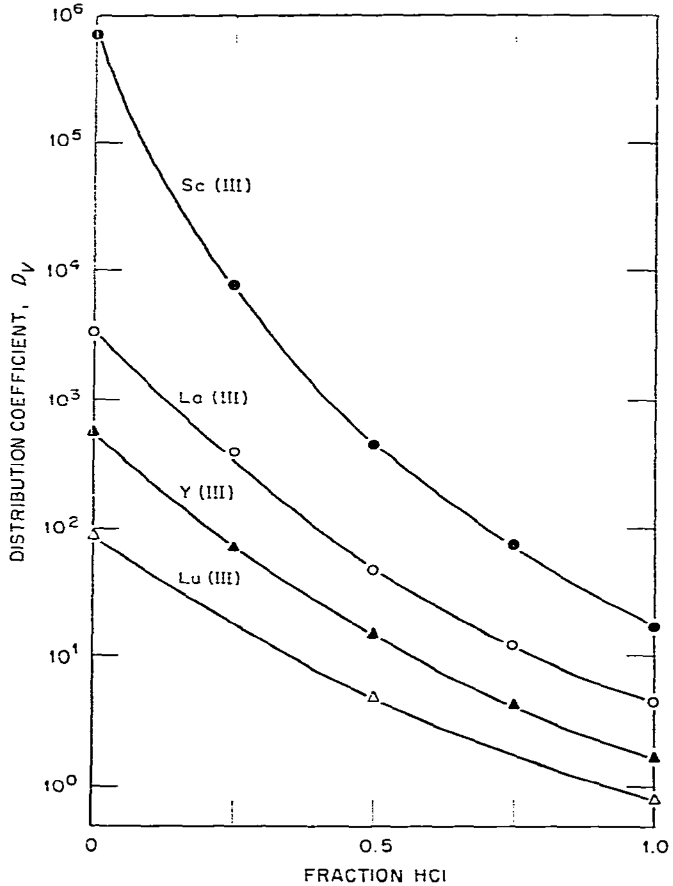

Fig. 6. Adsorption of Sc(III), Y(III) and trivalent rare earths from 9 *M* $HClO_4$–HCl mixtures on Dowex 50-X4 resin at 25°.

The strong adsorption of these trivalent elements, particularly at low F_{HCl}, permits their separation from weakly adsorbed elements as illustrated by Fig. 7. For this separation, a mixture of ^{91}Y, ^{46}Sc, ^{177}Lu, ^{140}La and two weakly adsorbed elements, ^{134}Cs and ^{131}Ba, initially in HCl or HNO_3 solution, was evaporated with *ca.* 0.5 ml of concentrated $HClO_4$. The residue (0.1 ml) was taken up in 0.5 ml of 8.5 *M* $HClO_4$–0.5 *M* HCl and added to a 5 cm × 0.25 cm² column of resin operated at 50° to improve exchange rates. On elution with the same solvent, Cs(I) and Ba(II) were eluted in sharp bands near 2 and 5 c.v., respectively. After their removal, Sc(III), Y(III) and the lanthanides [Lu(III) and La(III)] were removed (as a group) with 6 c.v. of 5 *M* HNO_3.

Trivalent actinides (Fig. 8). The adsorption functions for these elements resemble those for the lanthanides; Ac(III) and Am(III) are strongly adsorbed from 9

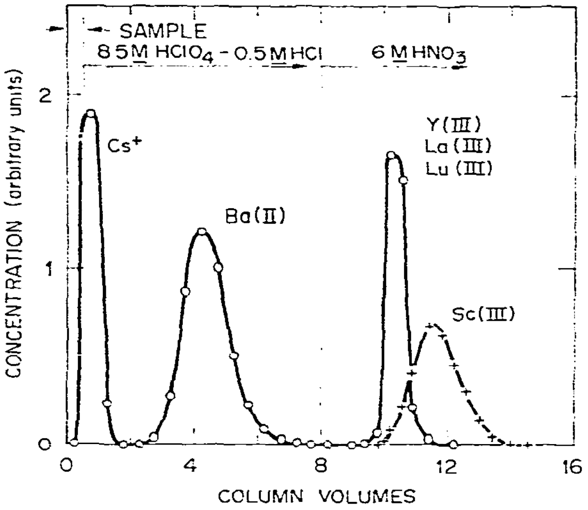

Fig. 7. Separation of Cs$^+$ and Ba(II) from Sc(III), Y(III) and lanthanides [La(III) and Lu(III)] by cation exchange on Dowex 50-X4 resin (0.25-cm^2 column) at 50°.

M HClO$_4$ ($D_v = 10^4$ and 2×10^3, respectively); in 9 *M* HCl, $D_v = 8$ and 1.2 respectively, for Ac(III) and Am(III).

As shown in Fig. 8, the adsorbability of Ac(III) and Am(III) in 9 *M* HClO$_4$–HCl mixtures decreases rapidly with increasing F_{HCl} to $D_v = 100$ and 12, respectively

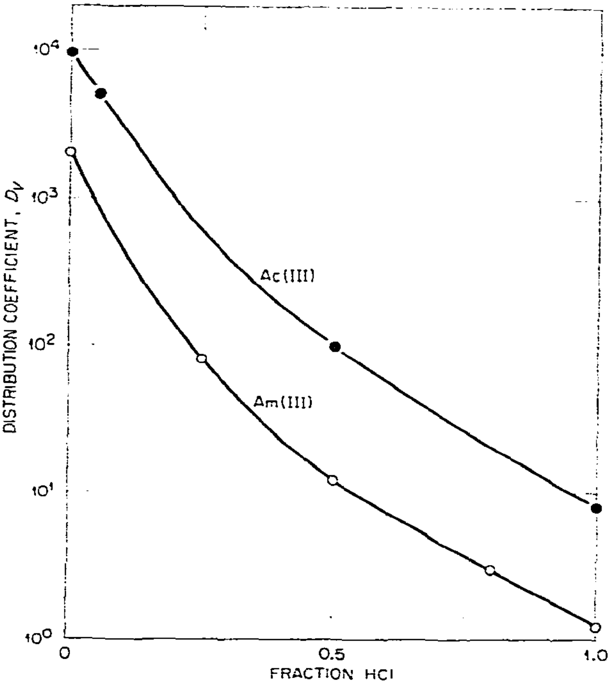

Fig. 8. Adsorption of Ac(III) and Am(III) from 9 *M* HClO$_4$–HCl mixtures on Dowex 50-X4 resin at 25°.

for 4.5 M $HClO_4$–4.5 M HCl mixtures. In separate experiments with small columns and with this acid mixture, Cm(III) eluted slightly before Am(III). One thus expects a systematic decrease in the adsorbability of actinides with increasing atomic number similar to that occurring with the lanthanides. The strong adsorption of the trivalent actinides at low F_{HCl} may be used to separate them as a group from weakly adsorbed elements.

Ti(IV), Zr(IV), Hf(IV) and Th(IV) (Fig. 9). These elements are strongly adsorbed from 9 M $HClO_4$ ($D_v > 10^3$); in 9 M HCl, they are weakly adsorbed (D_v *ca.* 1), except for Th(IV), for which $D_v = 28$. As shown in Fig. 9, the adsorbability in 9 M $HClO_4$–HCl mixtures decreases rapidly with increasing F_{HCl}, and at $F_{HCl} = 0.5$, $D_v = 3.7$, 22, 29 and 65 for Ti(IV), Zr(IV), Hf(IV) and Th(IV), respectively.

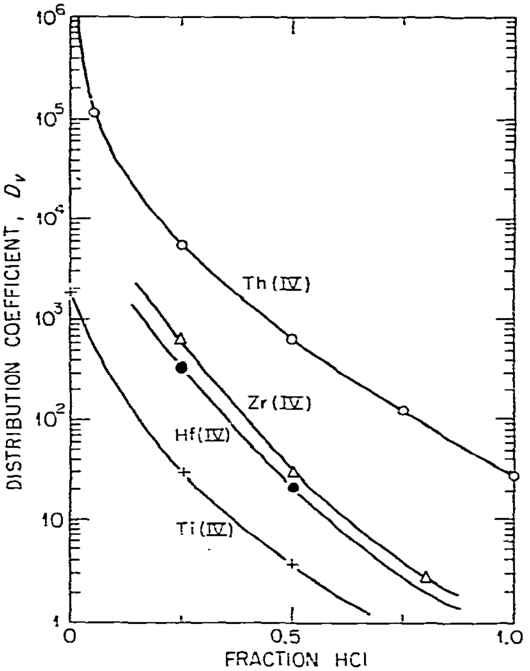

Fig. 9. Adsorption of Ti(IV), Zr(IV), Hf(IV) and Th(IV) from 9 M $HClO_4$–HCl mixtures on Dowex 50-X4 resin at 25°.

Nb(V), Ta(V) and Pa(V) (Fig. 10). These elements, even at tracer concentrations, hydrolyze in 9 M $HClO_4$ and adsorb erratically and irreversibly on cation exchangers. Reproducible behavior was obtained, however, when a strong complexing agent, *e.g.*, HF, was added to the solutions. By extrapolating adsorption data to low HF concentrations, we concluded[2] that the elements are very strongly adsorbed ($D_v > 10^3$) in 9 M $HClO_4$ solutions. In 9 M HCl, we found[2] that Nb(V), Ta(V) and Pa(V) are weakly adsorbed (D_v = *ca.* 1) and that slight adsorption occurs in 12 M HCl (D_v = *ca.* 2). Our data (obtained by the column method) do not agree with batch-equilibration measurements by Keller[9], who found distribution coefficients an order of magnitude larger than ours in 9–12 M HCl; the reason for this disagreement is not known.

In 9 M $HClO_4$-HCl mixtures, Ta(V) and Pa(V) at tracer concentrations ($<10^{-7}$ M) showed erratic adsorption behavior. Reproducible results were found with carrier-free Nb(V), (fission product ^{95}Nb), for which $D_v = 250$, 5.5 and 2 at F_{HCl} values of 0.025, 0.25, and 0.5, respectively.

A typical separation involving "carrier-free" Nb(V) (fission-product ^{95}Nb) is shown in Fig. 10. For this separation, a 9 M HCl–0.1 M HF solution containing the tracers ^{22}Na, ^{181}Hf, ^{95}Nb and ^{44}Ti–^{44}Sc was evaporated with 0.5 ml of concentrated $HClO_4$ to remove the volatile acids. The residue (*ca.* 0.1 ml) was taken up in 0.5 ml of 8.5 M $HClO_4$–0.5 M HCl, warmed for a few minutes, then added to a 0.28-cm^2 × 3-cm column of resin. On elution with 6.75 M $HClO_4$–2.25 M HCl ($F_{HCl} = 0.25$), Na^+ and Nb(V) appeared in the effluent in separate bands near 1.5 and 5.5 c.v., respectively. The Ti(IV) was removed with 5.4 M $HClO_4$–3.6 M HCl, Hf(IV) with 9 M HCl and Sc(III) with 4 M HCl–0.1 M HF. While Sc(III) also could have been removed with 3 M HCl where D_v is a minimum, removal is more rapid with HCl–HF mixtures through fluoride complexing. When similar column separations were attempted with samples containing 10^{-4} M Nb(V), part of the Nb(V) adsorbed very strongly on the column, presumably as a hydrolyzed species.

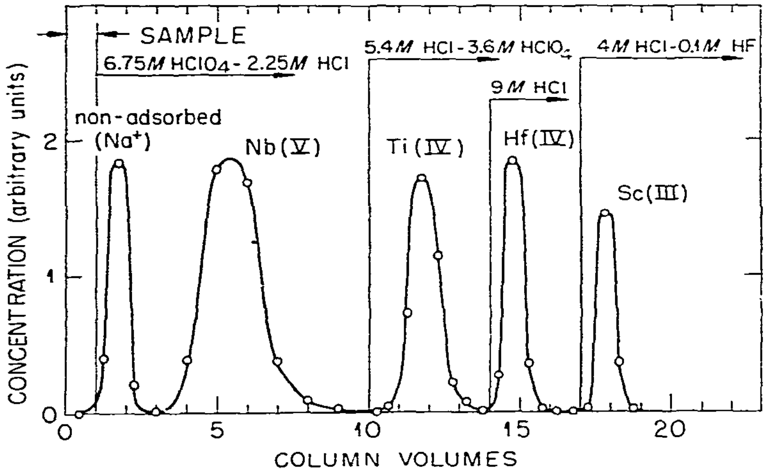

Fig. 10. Separation of non-adsorbed elements (Na^+), Nb(V), Ti(IV), Hf(IV) and Sc(III) by cation exchange on Dowex 50-X4 resin (2-cm column) at 25°.

Reproducible ion-exchange behavior was obtained with Nb(V), Ta(V) and Pa(V) in 9 M $HClO_4$–HCl mixtures that contained small amounts of HF; by extrapolating the data to zero HF concentration, at least limiting values for D_v were established. As in 9 M $HClO_4$ solutions[2], D_v for these elements in 8.5 M $HClO_4$–0.5 M HCl decreases rapidly with increasing HF concentration, and adsorbability becomes negligible at $M_{HF} >$ *ca.* 0.1. At $M_{HF} = 10^{-3}$, D_v values are all >15. The adsorbability of Ta(V) and Pa(V) appeared to decrease rapidly with F_{HCl}.

Mo(VI), W(VI) and U(VI) (Figs. 11 and 12). These elements are strongly adsorbed from 9 M $HClO_4$ ($D_v > 4 \times 10^2$) and very weakly from 9 M HCl ($D_v < 1$). As shown in Fig. 11, adsorbability decreases rapidly with increasing F_{HCl} and in 8.5 M $HClO_4$–0.5 M HCl ($F_{HCl} \approx 0.06$), D_v is 2, 3 and 55 for W(VI),

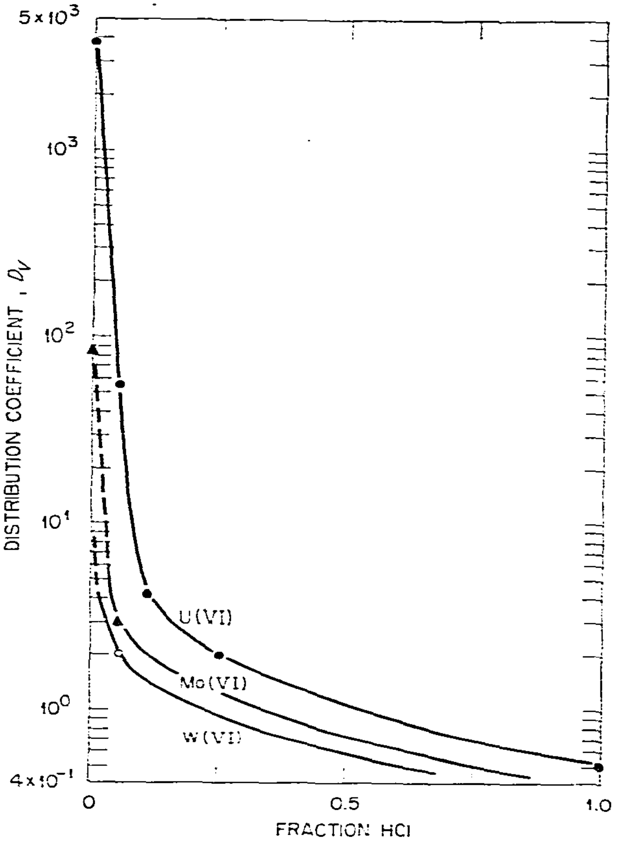

Fig. 11. Adsorption of W(VI), Mo(VI) and U(VI) from 9 *M* $HClO_4$-HCl mixtures on Dowex 50-X4 resin at 25°.

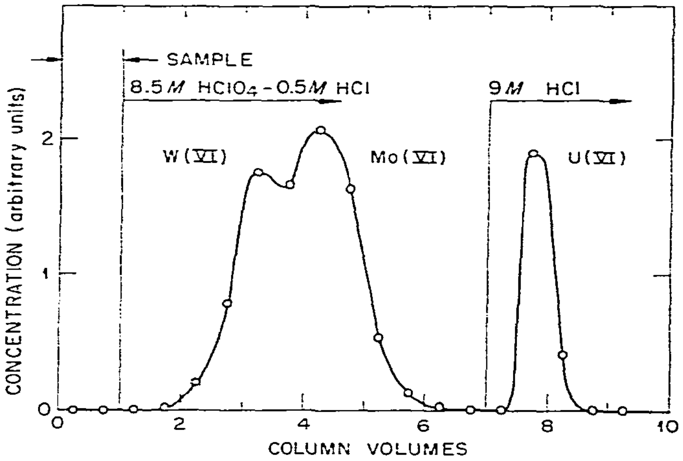

Fig. 12. Separation of W(VI) and Mo(VI) from U(VI) by cation exchange on Dowex 50-X4 resin (2-cm column) at 25°.

Mo(VI) and U(VI), respectively. At $F_{HCl} = 0.25$, adsorption of U(VI) becomes low ($D_v = 2$). Since U(VI) in 8.5 *M* $HClO_4$–0.5 *M* HCl solutions is more strongly adsorbed than Mo(VI) and W(VI), it may be separated from these elements; a typical separation is shown in Fig. 12.

A mixture of the tracers, ^{99}Mo–^{99}Tc, ^{186}W and 0.01 *M* U(VI) in HCl solution was evaporated with 0.5 ml of concentrated $HClO_4$ to remove HCl. Evaporation was continued a few minutes longer to reduce the sample volume and to fume off the 6-h ^{99}Tc daughter of ^{99}Mo. The residue, *ca.* 0.1 ml, was taken up in 0.5 ml of 8.5 *M* $HClO_4$-0.5 *M* HCl, warmed a few minutes to assure dissolution of possible Mo(VI) and W(VI) hydrolysis products, and added to a small column of Dowex 50-X4 resin. On elution with the same reagent, W(VI) and Mo(VI) were removed in overlapping elution bands with peak maxima at 3.2 and 4.2 column volumes, respectively; U(VI) was removed in a sharp band with 9 *M* HCl.

Fe(III), Ga(III), Au(III) and Sb(V) (Fig. 13). In 9 *M* $HClO_4$, Fe(III) and Ga(III) are significantly adsorbed ($D_v > 100$). The adsorption behavior of Au(III) and Sb(V) in 9 *M* $HClO_4$ is erratic, presumably because both elements form troublesome hydrolysis products. In 9 *M* HCl, Au(III) and Sb(V) are strongly adsorbed ($D_v = 120$ and 2,000, respectively).

In 9 *M* $HClO_4$–HCl mixtures, Fe(III), Ga(III), Au(III) and Sb(V) are significantly adsorbed at all HCl fractions (Fig. 13). D_v values tend to level out in the region $F_{HCl} = 0.1$ to 0.8 and at $F_{HCl} = 0.5$, $D_v = 155$, 64, 16 and 590 for Fe(III), Ga(III), Au(III) and Sb(V), respectively.

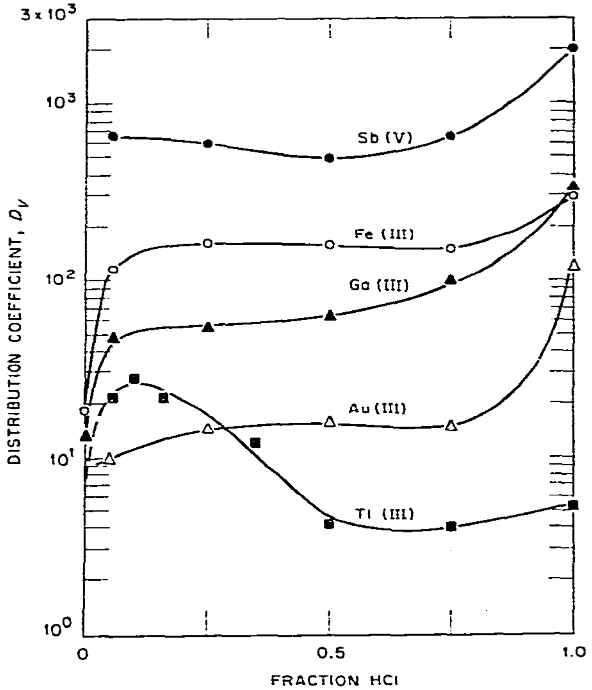

Fig. 13. Adsorption of Fe(III), Ga(III), Au(III), Tl(III) and Sb(V) from 9 *M* $HClO_4$–HCl mixtures on Dowex 50-X4 resin at 25°.

Since these elements may be adsorbed over almost the entire range of HCl concentration in 9 *M* $HClO_4$–HCl mixtures, numerous separations are possible in these media. A typical separation involves the elements Fe(III), U(VI) and Cs(I). A mixture of the tracers, ^{59}Fe, ^{237}U and ^{134}Cs in 8.5 *M* $HClO_4$–0.5 *M* HCl was added to a 3 cm × 0.28 cm^2 column of Dowex 50-X4 resin that had been pre-treated with the same solvent. Elution with 8.5 *M* $HClO_4$–0.5 *M* HCl removed Cs(I); U(VI) was then eluted in a sharp band with 9 *M* HCl, and Fe(III) with 3 *M* HCl.

Zn(II), Cd(II) and Hg(II). In 9 *M* $HClO_4$, Zn(II), Cd(II) and Hg(II) are significantly adsorbed ($D_v = 1.8$, 17 and 7, respectively), while in 9 *M* HCl adsorbability is negligible. In 9 *M* $HClO_4$–HCl mixtures, D_v decreases very rapidly with increasing F_{HCl} and becomes negligible at $F_{HCl} \geqslant 0.05$.

In(III) and Tl(III). From 9 *M* $HClO_4$, In(III) is slightly adsorbed ($D_v = 9.5$); in 9 *M* HCl, $D_v < 1$. In 9 *M* $HClO_4$–HCl mixtures, D_v of In(III) decreases rapidly with increasing F_{HCl} and becomes less than unity at $F_{HCl} \geqslant 0.05$.

Tl(III) appears to be weakly adsorbed from 9 *M* $HClO_4$, (D_v = *ca.* 1), but the data are in doubt because of possible reduction of Tl(III) to Tl(I) by the resin[2]. In 9 *M* HCl solutions containing chlorine as oxidizing agent, Tl(III) is significantly adsorbed ($D_v = 5.3$). In 9 *M* $HClO_4$–HCl mixtures (see Fig. 13), D_v decreases from a maximum of 28 near $F_{HCl} = 0.1$ to a minimum of 2 near $F_{HCl} = 0.8$ and then increases slightly. Below $F_{HCl} = 0.1$, the adsorbability of Tl(III) appears to decrease with decreasing F_{HCl}.

V(IV), Mn(II), Pb(II) and Bi(III). V(IV) and Mn(II) are adsorbed from 9 *M* $HClO_4$ with $D_v = 21$ and 19, respectively; both elements are weakly adsorbed from 9 *M* HCl ($D_v < 1$). The adsorbabilities of V(IV) and Mn(II) in 9 *M* $HClO_4$–HCl mixtures decrease rapidly with increasing F_{HCl} and at $F_{HCl} = 0.06$, $D_v = 3.2$ and 2.0, respectively.

In 9 *M* $HClO_4$, Pb(II) and Bi(III) are significantly absorbed ($D_v = 19$ and 860, respectively); in 9 *M* HCl, adsorbability is negligible. In 9 *M* $HClO_4$–HCl mixtures, D_v of Pb(II) and Bi(III) decrease very rapidly with increasing F_{HCl} and becomes negligible at $F_{HCl} \ll 0.05$.

Np(VI) and Pu(VI). Np(VI) and Pu(VI) are strongly adsorbed ($D_v > 100$) from 9 *M* $HClO_4$ and are negligibly adsorbed from 9 *M* HCl. In 9 *M* $HClO_4$–HCl mixtures, the adsorption functions of Np(VI) and Pu(VI) are similar to that of U(VI) (Fig. 11). Thus, U(VI), Np(VI) and Pu(VI) are sufficiently strongly adsorbed from 8.5 *M* $HClO_4$–0.5 *M* HCl ($F_{HCl} = 0.056$) to permit their separation as a group from weakly adsorbed elements. A mixture of the tracers, ^{237}U, ^{238}Np, ^{239}Pu, ^{134}Cs and ^{133}Ba, initially in 9 *M* HCl, was evaporated with 0.5 ml of 9 *M* $HClO_4$. The residue (*ca.* 0.1 ml) was taken up in 1 ml of 8.5 *M* $HClO_4$–0.5 *M* HCl, treated with Cl_2 gas to ensure oxidation of Np and Pu to the (VI) state and added to a 5 cm × 0.25 cm^2 column of Dowex 50-X4 resin that had been pre-treated with 8.5 *M* $HClO_4$–0.5 *M* HCl–Cl_2 solution; the separation was carried out at 50° to improve exchange rates. On elution with the same acid mixture, ^{134}Cs and ^{133}Ba appeared in the effluent in separate elution bands near 1 and 4 c.v., respectively, while U(VI), Np(VI) and Pu(VI) remained adsorbed; they were eluted together with 9 *M* HCl.

Some comments regarding species in solution

Analysis of the adsorption functions in $HClO_4$–HCl mixtures in terms of complexing reactions of the metals in the aqueous phase is difficult at high ionic strength, except in special cases. Problems arise because there are no simple ground rules by which variations of activity coefficients in either phase can be predicted, even if the compositional changes are confined to media of constant ionic strength. The assumption that activity coefficients do not vary with composition at constant ionic strength is only an approximation even in dilute electrolyte solutions. As we have pointed out earlier[10], it is already of questionable validity at moderate ionic strengths, and it becomes totally inadequate at high ionic strength.

The most widely applicable mixing rule regarding activity coefficients is Harned's rule[6], which states that, in mixtures of constant ionic strength (here molality) log $\gamma_\pm$ varies linearly with composition (here F_{HCl} or F_{HClO_4}). If Harned's rule is applicable to both phases, a linear dependence of log D on F_{HCl} would be expected if no complexing occurs. This seems to be approximately the case for the alkaline earths (Fig. 4), the lanthanides (Fig. 6) and Ac(III) and Am(III) (Fig. 8). Qualitatively, a slight concavity is expected, since the measurements were carried out at constant molarity rather than constant molality. In either case, we consider the deviation from linearity too small to warrant analysis in terms of hypothetical complexing reactions.

We have touched on this problem earlier in this paper in connection with the discussion of Fig. 1. There we expressed the opinion that chloride complexing is not indicated if K/Γ varies similarly with activity of water in HCl and $HClO_4$ solutions. Only if the difference in slopes in the two media is large would assumption of chloride complexing be reasonable. However, even then a reasonably accurate evaluation of the extent of complexing would be difficult, except in those cases where relatively small amounts of hydrochloric acid in $HClO_4$–HCl mixtures would cause a dramatic decrease in adsorbability. A particularly favorable example, U(VI), is shown in

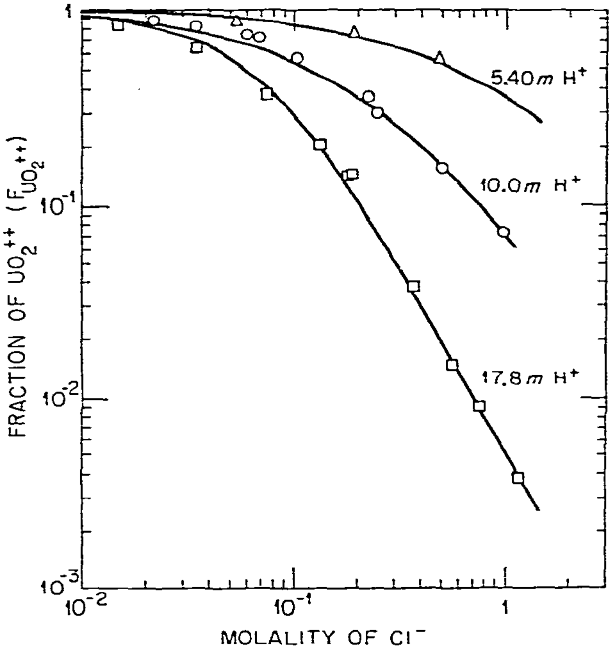

Fig. 14. Chloride complexing of UO_2^{2+} in HCl–$HClO_4$ mixtures.

Fig. 11. For this element, distribution coefficients drop (in 9 *M* $HClO_4$–HCl mixtures) by several orders of magnitude before the HCl fraction (F_{HCl}) reaches 10%.

We have examined this case in somewhat greater detail, measuring distribution coefficients in three systems of constant ionic strength [5.40, 10.0, and 17.8 *m* (moles of acid/kg of water)]. The HCl concentration, m_{HCl}, in these mixtures was varied from about 10^{-2} to *ca.* 1 except for the most dilute solution where the maximum value of $m_{HCl} = 0.5$. If we assume that with these small maximum values of F_{HCl} the activity-coefficient ratio for the ion-exchange equilibrium is approximately constant, and if we further assume that the complexed species do not adsorb significantly, we can compute F_{UO_2}, the fraction of uncomplexed UO_2^{2+}, from the ratio of the observed distribution coefficients in the mixtures to that in pure $HClO_4$ solutions[10]. The results of the computation are given in Fig. 14. The uncomplexed fraction of UO_2^{2+}, which only decreases moderately at the lower ionic strength, decreases dramatically at the highest ionic strength. This is consistent with the frequent observation that complexing becomes much more extensive as the ionic strength increases (see also ref. 10).

It is apparent from inspection of Fig. 14 that, near $m_{Cl} = 1$ at an ionic strength of 17.8, the slope of the log–log plot is approximately −2, which implies that the reaction to form the complex UO_2Cl_2 has become dominant. There seems to be no evidence yet for the formation of negatively charged species, which occur at higher chloride concentrations[10].

We can estimate from the dependence of F_{UO_2} on m_{Cl} the concentration quotients of the pertinent complexing reactions by the relationship

$$\left(\frac{1}{F_{UO_2}} - 1\right) = \Sigma k_{0i}^m \, (m_{Cl})^i \tag{4}$$

which is analogous to the relationship that we earlier derived for complexing reactions with anion exchangers[10]. In equation 4, k_{0i}^m is the concentration quotient for the complexing reactions. In our case only

$$k_{01}^m = \frac{m_{UO_2Cl}}{m_{UO_2}m_{Cl}} \tag{5}$$

and

$$k_{02}^m = \frac{m_{UO_2Cl_2}}{m_{UO_2}m_{Cl}^2} \tag{6}$$

seem of interest. From an analysis of the curve in Fig. 14, we find that $k_{01}^m \approx 10$, and $k_{02}^m \approx 180$ at a total ionic strength (I) of 17.8. At $I = 10.0$, k_{02}^m is very much smaller; we estimate $k_{02}^m \approx 11$ and $k_{01}^m \approx 5$. At $I = 5.4$, the results do not permit meaningful calculation of k_{02}^m: they are consistent with a value of $k_{01}^m \approx 1.6$. Thus, while both k_{01}^m and k_{02}^m increase considerably with I, the dependence of k_{02}^m on I is, as expected[10], very much larger than that of k_{01}^m.

ACKNOWLEDGEMENTS

Dr. Takeo Murase carried out the work on U(VI) chloride complexing at constant ionic strength. We are indebted to him for permission to report his work here.

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