[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Anion-exchange Studies. XXVII. Adsorbability of a Number of Elements in HCl–HF Solutions[1,2]

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RECEIVED JULY 1, 1959

In an extension of previous studies on adsorption by anion exchangers of metallic elements from HCl–HF solutions, an additional nineteen elements including some from groups 2, 3, 4, 5 and transition elements, were studied at constant 1 *M* HF and variable HCl concentration (0.1 to 11 *M*). The data are compared with adsorbabilities in HCl solutions, not containing HF, most of which were previously published, though for some elements new data are reported here (Fe(III), Tl(III), Sn(II), Sn(IV), Sb(III), Sb(V)). A large group of elements which are non-adsorbable from HCl solutions are also not adsorbed from HCl–HF mixtures. This group includes even such highly charged ions as Al(III), Y(III), Rare Earths (Eu(III)), Th(IV) and V(IV), though Be(II) shows some adsorption at low HCl concentration in the presence of 1 *M* HF. The adsorption functions of many elements adsorbable from HCl solutions show little change on addition of HF. For others, the adsorption functions may be substantially altered as shown earlier for a number of elements of the 4th, 5th and 6th groups and shown here for Sc(III), Ti(IV), Fe(III), Ga(III), Ge(IV), Sn(II) and (IV) and Sb(III) and (V). From the adsorption functions in HCl and HCl–HF estimates of the extent of fluoride complexing are obtained. Application of the adsorption data to separations is discussed and illustrated with typical cases.

The anion-exchange behavior of the metallic elements in HCl solutions has been systematically studied at this Laboratory and some of the results were summarized recently.[3] Concurrent with these studies, adsorbabilities of a number of elements from HCl–HF media also were investigated. This medium was originally selected[4] because it appeared to be a suitable solvent for those elements of the fourth and fifth groups (*e.g.*, Zr(IV), Hf(IV), Nb(V), Ta(V) and Pa(V)) which tend to hydrolyze, polymerize or precipitate even in fairly concentrated acid solution; HCl–HF solutions were found to be suitable media for reversibly handling these elements and for separating them efficiently from each other.

To make the HCl–HF system more generally useful for separations and to obtain information on fluoride complexing, studies later were extended to include Mo(VI), W(VI), U(IV) and U(VI).[5] In the present paper results for nineteen additional elements (Be, Al, Sc, Y, Rare Earths (Eu), Th, Ti, V, Fe, Zn, Ga, In, Tl, Ge, Sn, Pb, As, Sb and Bi) are reported. These studies were carried out at constant 1 *M* HF concentration and variable HCl concentration ($0.1 \leqslant M\text{HCl} \leqslant 11$). The adsorption functions in HCl–HF are compared with those obtained in HCl solution (no HF) with the same resin to permit a more general evaluation of these systems for separations and study of complexing reactions.

Experimental

The ion exchanger was from the same batch of strongly basic quaternary amine resin (Dowex-1, 10% DVB, 170–220 mesh) with which most of the earlier studies were carried out.[3] It was used in the chloride form and air-dried for convenience in handling. All distribution coefficients D (amount per kg. resin/amount per liter of solution), however, refer to the weight of the chloride form of the resin dried to constant weight over "Anhydrone" at 60° in a vacuum desiccator.

Adsorbabilities were measured by column elution, preloaded column or equilibration methods. In the column elution method, aliquots of solutions containing the various metals were added to small columns which had been pretreated with the appropriate HCl–HF solutions, and then eluted with the same electrolyte solutions. From the number of column volumes at which the metal appears in maximum concentration in the effluent, the volume distribution coefficient, D_v (amount adsorbed per liter of bed/amount per liter of solutions), was computed. This method is relatively rapid for measuring values of $D_v <$ *ca.* 10. If distribution coefficients were substantially larger, the batch equilibration method, being more rapid, was preferred. In this method, measured amounts of resin and solution were agitated together until there was no significant change in metal concentration in solution with time. Usually a 24-hour period was ample, though for some of the Sb(V) experiments, several days were needed. From analyses of the solution phase before and after equilibration, the weight distribution coefficient D was calculated. Values of D were converted to volume distribution coefficients (D_v) by the relationship $D_v = D\rho$, where ρ is the bed density (*ca.* 0.45 kg./l. for the resin used here). For measurement of very high distribution coefficients the preloaded column technique[2c,3b] was used in some cases. A known amount of resin was uniformly loaded with the element of interest. It was placed into a column and eluting solution passed through it. Distribution coefficients were computed from the concentrations of metal in the bed and in the effluent.

Radiometric methods were used for most metal analyses. Aliquots of solutions containing gamma emitting tracers were counted in a well-type scintillation counter. For analysis of solutions containing the pure beta-emitter Tl^{204}, aliquots were evaporated on stainless steel plates and counted with a beta proportional counter.

The tracers Sc^{46} (85d), Y^{91} (58d), Eu^{155} (1.7y), Zn^{65} (245d), Fe^{59} (45d), In^{114} (49d), Tl^{204} (4.1y), Sn^{113}–In^{113m} (112d–1.75h), Sb^{124} (60d) and Th^{234} (UX_1, 24.1d) were obtained as analyzed "stock" solutions from the ORNL Isotopes Division. A Pb^{210}–Bi^{210} (RaD–RaE, 19.4y–5.0d) tracer was isolated from a residue containing Ra^{226} decay products.[6] The Ga^{72} (14.2h) and Ge^{77}–As^{77} (12h–38.8h) tracers were prepared by irradiating Ga_2O_3 and GeO_2 in the ORNL Low Intensity Test Reactor (LITR). After irradiation, the Ga_2O_3 was dissolved in concentrated HCl and the GeO_2 in 1 *M* NaOH. Half-life measurements on portions

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, operated by the Union Carbide Corporation, Oak Ridge, Tennessee. Presented in part at the 131st Meeting of the Am. Chem. Soc., Miami, Florida, April, 1957.

[2] Previous papers: Anion-exchange Studies (a) XXIV, K. A. Kraus and F. Nelson, Symposium on the Structure of Electrolytes, W. J. Hamer, Editor, Meeting of the Electrochemical Society, Spring 1957, John Wiley and Sons, 1959; (b) XXV, Y. Marcus and F. Nelson, *J. Phys. Chem.*, **63**, 77(1959); (c) XXVI, K. A. Kraus, R. J. Raridon and D. L. Holcomb, *J. Chromatography* (in press).

[3] (a) K. A. Kraus and F. Nelson, "Anion Exchange Studies of the Fission Products," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, P/837, Vol. VII, p. 113, Session 9B.1, United Nations (1956). (b) K. A. Kraus and F. Nelson, "Metal Separations by Anion Exchange" in Symposium on Ion Exchange and Chromatography in Analytical Chemistry (June, 1956), Am. Soc. for Testing Materials, Special Technical Publication No. 195.

[4] K. A. Kraus and G. E. Moore, THIS JOURNAL, (a) **71**, 3263, 3855 (1949); (b) **73**, 9, 13, 2900 (1951); (c) **77**, 1383 (1955).

[5] K. A. Kraus, F. Nelson and G. E. Moore, *ibid.*, (a) **77**, 3972 (1955); (b) **78**, 2692 (1956).

[6] We are indebted to Drs. P. S. Rudolph and B. H. Ketelle for supplying the RaD–RaE tracers in a separated state.

of these "stock" solutions showed the tracers to be of satisfactory purity.

The Be^7(53.6d), V^{48}(16.1d) and Bi^{207}(8y) tracers were prepared by proton irradiation[7] of LiF, TiO_2 and Pb metal. The Be^7 tracer was separated from the LiF target by a coprecipitation method, after dissolving the target in concentrated nitric acid. The target dissolved very slowly, even on heating; presumably fluoride is volatilized during dissolution. After cooling the solution, a small amount of Al(III) was added, which was then precipitated with ammonia. The precipitate, which carried essentially all the activity, was washed and dissolved in 1 *M* HF–0.01 *M* HCl. The Be^7 was separated from the aluminum and recovered in a carrier-free state by anion-exchange essentially as described in Section 2.1. Gamma ray spectrometry showed the separated tracer to be radiochemically pure.

A cation-exchange method was devised to separate and purify the V^{48} tracer (see also Section 2.2). The TiO_2 target was dissolved in 1 *M* HF–0.1 *M* HCl and the solution added to a small column of Dowex-50 × 8. In preliminary experiments, it was found that Ti(IV) is not adsorbed under these conditions, while V(IV) was found to be adsorbed. However, part of the vanadium was not adsorbed, possibly because it was present as a (negatively charged?) species of V(V). With the addition of a small amount of $TiCl_3$ solution as reductant, however, the V^{48} activity could be quantitatively adsorbed by the cation exchanger and thus separated from titanium. The V^{48} was eluted with 1.5 *M* HCl and by γ-ray spectrometry was found to be radiochemically pure.

Bi^{207} was separated and purified by anion exchange[8] after dissolving the lead target in HNO_3.

All tracers, except Sn^{113} and Tl^{204}, were of sufficiently high specific activity so that in the adsorption studies loading of the resin was less than 1 or 2% of its capacity. Resin loading ranged from 1 to 10% for Sn(II), 1 to 35% for Sn(IV) and about 4% for Tl(III). These loadings were computed on the assumption that the adsorbed complexes of Sn(II) and Sn(IV) have charge −2, while that of Tl(III) has charge −1. Since distribution coefficients decrease significantly with loading and since in these experiments loading increases with adsorbability, the high distribution coefficients for these elements are not strictly comparable with those where loading was low.

Tracers of Al and Ti were not conveniently available and hence experiments were carried out with *ca.* 10^{-3} *M* solutions of these elements. In the case of Al, which does not absorb strongly, analysis was by spot testing of successive aliquots of the effluent from the column. Drops were collected on a platinum strip and then evaporated to dryness. The appearance of the solid residues indicated the volume at which Al appeared in maximum concentration in the effluent. Analysis for Ti(IV) was carried out polarographically (nitrogen atmosphere). The solutions were fumed with H_2SO_4 to remove HF and the final H_2SO_4 concentration adjusted to *ca.* 1 *M*. Although the reduction waves are probably irreversible in this medium,[9] they appeared satisfactory for analytical purposes.

For analysis of Sn(II) in HCl, polarography was chosen in preference to a tracer technique, since the former would also reveal presence of significant amounts of Sn(IV). Solutions of Sn(II) (*ca.* 10^{-3} *M*) were placed into a polarographic cell under a nitrogen atmosphere and analyzed. Weighed amounts of resin were added and the mixture stirred with nitrogen for approximately 1 hour. After permitting the resin to settle, the solution was again analyzed polarographically. Distribution coefficients were calculated from the analyses before and after addition of resin. With the precautions taken to exclude oxygen from the system no difficulties from formation of Sn(IV) were encountered. Since the stirring times were very short in these experiments the computed distribution coefficients must be considered lower limits.

Adsorbability of Sn(II) from HCl–HF mixtures is relatively low and distribution coefficients readily can be determined by the column technique. Partial oxidation of Sn(II) to Sn(IV) in the column would not lead to serious errors because the adsorbabilities of the two oxidation states differ widely. Hence in these measurements the tracer–column technique was used instead of the more cumbersome polarographic method. Small aliquots containing 0.01 to 0.05 *M* Sn(II) and Sn^{113} tracer were added to the columns and immediately eluted without taking precautions to exclude air.

Experiments with solutions containing HF were carried out in plastic equipment. Polyethylene flasks and "Lusteroid" test-tubes were used; columns and pipets were made from polyethylene tubing. All experiments were carried out in an air conditioned room at 25 ± 1°.

Results and Discussion

1. Adsorption from HCl and HCl–HF Solutions.—Adsorption data for the various elements are summarized in Figs. 1 to 5 as plots of the logarithms of the weight distribution coefficients *D vs.* molarity *M* of HCl. The solid lines refer to adsorption functions in HCl–HF mixtures at constant 1 *M* HF; the dashed curves refer to HCl solutions. Experimental points are shown for new data. Curves without experimental points are reproduced from earlier publications.[10]

1.1. Beryllium (Fig. 1).—Adsorbability of Be(II) is negligible from HCl solutions.[10b] In the presence of 1 *M* HF, Be(II) is significantly adsorbed only from dilute HCl solutions. The distribution coefficients decrease from $D = 17$ near 0.05 *M* HCl–1.0 *M* HF to $D = 1$ near 0.5 *M* HCl–1 *M* HF. For *M* HCl > 1 adsorbability from 1 *M* HF is essentially negligible.

1.2. Aluminum, Scandium (Fig. 1), Yttrium and Rare Earths.—Adsorbability of Al(III), Y(III) and the trivalent rare earths is negligible at all HCl concentrations; Sc(III), which does not absorb from dilute HCl solutions, is slightly adsorbed from concentrated HCl ($D \approx 2$ in 12 *M* HCl).[10b] Study of most of these elements in HF solutions is complicated by the insolubility of the fluorides; thus with Y(III) erratic results have been obtained in dilute HCl, even at tracer concentrations, possibly because of partial precipitation in the resin phase. Aside from the solubility problem it appears that Al(III), Y(III) and Eu(III), a typical rare earth, are not adsorbed from solutions containing 1 *M* HF and 0.1 to 11 *M* HCl. Some adsorption was found for Sc(III); thus in 0.1 *M* HCl–1 *M* HF, $D \approx 6$ was found, with adsorbability decreasing to $D \leqslant 1$ above 1 *M* HCl.

1.3. Titanium (Fig. 2).—Adsorption of Ti(IV) from HCl becomes significant near 9 *M* HCl and rises rapidly with increasing HCl concentration.[10b] Below *ca.* 9 *M* HCl, difficulties resulting from hydrolytic reactions of Ti(IV) may be encountered. These difficulties may be circumvented by addition of HF which strongly complexes Ti(IV). Extensive complexing by F^- is also indicated by the marked effect of HF on the adsorption function of Ti(IV). In 1 *M* HF, Ti(IV) is strongly adsorbed from dilute HCl solutions ($D \approx 150$ in 0.3 *M* HCl); *D* decreases with increasing HCl concentration to

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[7] We are indebted to Dr. J. L. Need of the ORNL Cyclotron group (Electronuclear Research Division) for these irradiations.

[8] See Ref. 10c.

[9] See *e.g.*, I. M. Kolthoff and J. J. Lingane, "Polarography," Second Edition, Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1952, p. 442.

[10] (a) Zn(II): K. A. Kraus and G. E. Moore, This Journal, **75**, 1460 (1953); (b) Al(III), Ga(III), In(III), Tl(III), Be(II), V(IV), Ti(IV), Sc(III), Rare Earths(III): K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954); (c) Pb(II), Bi(III): F. Nelson and K. A. Kraus, This Journal, **76**, 5916 (1954); (d) Ge(IV), As(III), As(V): F. Nelson and K. A. Kraus, *ibid.*, **77**, 4508 (1955); (e) Th(IV), Sn(IV): K. A. Kraus, G. E. Moore and F. Nelson, *ibid.*, **78**, 2692 (1956).

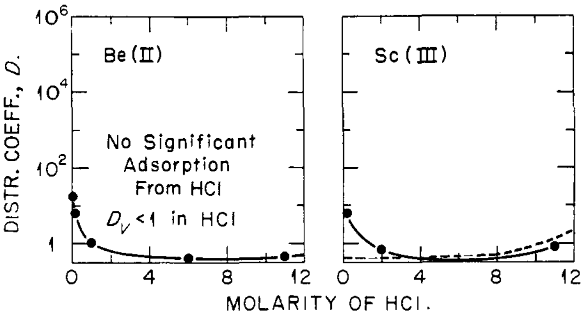

Fig. 1.—Adsorption of beryllium and scandium from HCl and HCl-HF solutions (1 *M* HF): ------ HCl; -●-, HCl-HF.

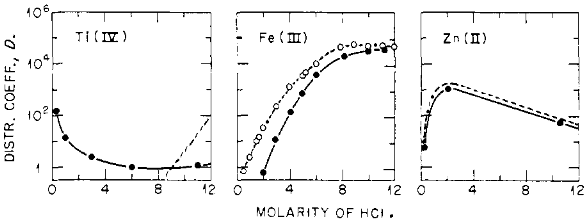

Fig. 2.—Adsorption of titanium, iron and zinc from HCl and HCl-HF solutions (1 *M* HF); ------ and ---○---, HCl; -●-, HCl-HF.

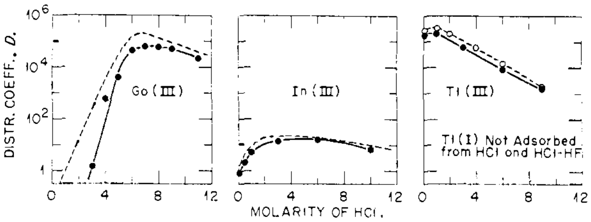

Fig. 3.—Adsorption of gallium, indium and thallium from HCl and HCl-HF solutions (1 *M* HF); ------ and ---○---, HCl; -●-, HCl-HF.

$D \approx 6$ in 3 *M* HCl and $D \approx 1$ in 6 *M* HCl; above this concentration *D* remains low. Similar adsorption studies with Ti(IV) in HCl-HF mixtures have been reported by Hague, Brown and Bright.[11] In the region of HCl concentrations where the measurements overlap, our data are in good agreement with theirs.

1.4. Thorium.—Adsorption of Th(IV) from HCl solutions is negligible.[10e] While thorium fluoride is quite insoluble, no difficulties were found in measurements at tracer Th(IV) concentrations in media containing 1 *M* HF and 0.1 to 11 *M* HCl. Under these conditions adsorption of Th(IV) was negligible.

1.5. Vanadium.—V(IV) is not appreciably adsorbed from HCl solutions,[10b] and presence of HF in amounts up to 1 *M* does not affect the adsorbability significantly; for 1 *M* HF solutions containing 0.1 to 11 *M* HCl, *D* is less than unity.

Partial, but irreproducible, adsorption of vanadium was observed from dilute HCl solutions containing 1 *M* HF and Cl_2 as oxidant. In a typical experiment, an aliquot containing V^{48}, 0.25 *M* HCl-1 *M* HF, and Cl_2 was added to a small column. On elution with the same medium, about 5% of the vanadium appeared within the first column volume in a rather broad band which tailed badly. Presumably, the remaining vanadium is adsorbed as a V(V) fluoride complex which is reduced slowly (tailing on elution) to non-adsorbable V(IV) species.

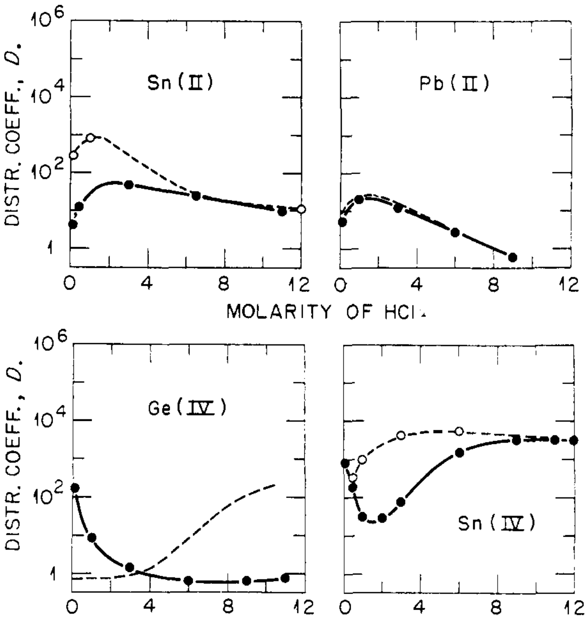

Fig. 4.—Adsorption of germanium, tin and lead from HCl and HCl-HF solutions (1 *M* HF): ------ and ---○---, HCl; -●-, HCl-HF.

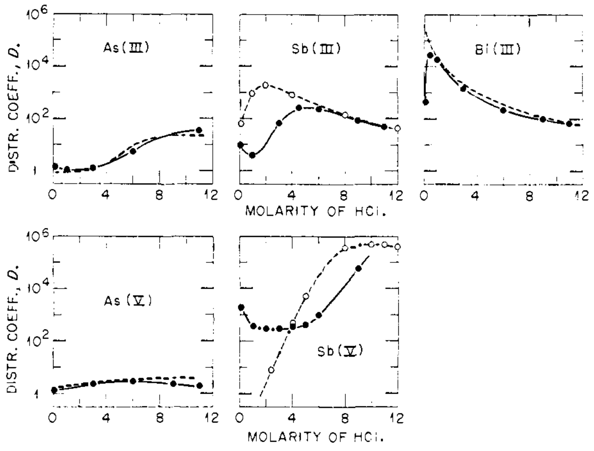

Fig. 5.—Adsorption of arsenic, antimony and bismuth from HCl and HCl-HF solutions (1 *M* HF); ------ and ---○---, HCl; -●-, HCl-HF.

1.6. Iron (Fig. 2).—As first reported by Moore and Kraus,[12] Fe(III) can be adsorbed strongly from HCl solutions; adsorbability becomes significant near 1 *M* HCl and rises rapidly with increasing HCl concentration. Later, in a more detailed study it was shown that the adsorption function has a broad maximum with $D = ca.\ 6 \times 10^4$ near 9 *M* HCl; adsorbability decreases slightly between 9 and 12 *M* HCl. These experimental data are shown in Fig. 2 although they had earlier

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[11] (a) J. L. Hague, E. D. Brown and H. A. Bright, *J. Research Natl. Bur. Standards*, **53**, 261 (1954). See also (b) J. L. Hague and L. A. Machlan, *ibid.*, **62**, 53 (1959).

[12] G. E. Moore and K. A. Kraus, THIS JOURNAL, **72**, 5792 (1950).

been summarized in a table of adsorption functions in HCl solutions.[3a]

In the presence of 1 M HF the adsorption function of Fe(III) has the same general shape as for HCl solutions and both tend to merge at high HCl concentrations. However, with decreasing HCl concentration the adsorption functions in the two media show increasing divergence; thus $D \approx 1$ in 2 M HCl–1 M HF while $D \approx 35$ in 2 M HCl in the absence of HF. In 1 M HF adsorption of Fe(III) remains negligible at least down to 10^{-2} M HCl in marked contrast to the behavior of many other elements which form relatively strong fluoride complexes.[5a]

1.7. **Zinc** (**Fig. 2**).—Adsorbability of Zn(II) increases with increasing M HCl from $D = 1$ near 0.01 M HCl to a maximum $D = 1800$ near 2 M HCl; at high HCl concentrations D decreases to $D = 55$ near 12 M HCl.[10a] Presence of 1 M HF has remarkably little effect on the adsorbability of Zn(II) at all HCl concentrations studied ($0.1 \leqslant M$ HCl $\leqslant 11$). The adsorption functions in the two media parallel each other closely; the small and apparently constant difference in log D between the two curves in Fig. 2, if significant, presumably reflects small differences of activity coefficients in the two media.

1.8. **Gallium** (**Fig. 3**).—For HCl solutions, distribution coefficients are essentially negligible below 1 M HCl, increase rapidly with increasing HCl concentration to a maximum $D = 2 \times 10^5$ near 7 M HCl and then decrease to $D = 3 \times 10^4$ in 12 M HCl.[10b] The effect of HF on the adsorption function of Ga(III) in HCl is similar to that on Fe(III). At high HCl concentrations the distribution coefficients in HCl and HCl–HF solutions tend to approach each other asymptotically, at low HCl concentrations the two curves diverge with the HCl–HF curve always lying below the HCl curve. As in the case of Fe(III), for M HCl < 3, and at least down to 0.1 M HCl, there is no evidence for a new adsorption region in the presence of 1 M HF.

1.9. **Indium** (**Fig. 3**).—Distribution coefficients for In(III) are relatively low in dilute HCl solutions; they increase from $D = 1$ near 0.1 M HCl to a broad maximum near 4 M HCl where $D = 23$. Above 4 M HCl, D decreases with increasing M HCl to $D = 7$ in 12 M HCl.[10b] Presence of 1 M HF, as in the case of Zn(II), has very little effect on the adsorption function of In(III), the curves in HCl and HCl–HF paralleling each other closely with the HCl–HF curve slightly below the HCl curve.

1.10. **Thallium** (**Fig. 3**).—We have reported[10b] earlier that Tl(I) is slightly adsorbed from HCl solutions. In a re-examination, adsorption of Tl(I) from HCl solutions (0.1 to 12 M) was found to be negligible at Tl(I) concentrations of the order of 10^{-3} M, in disagreement with the results of Horne[13] who reported strong adsorption of Tl(I) from HCl solutions. At very low Tl(I) concentrations (tracer Tl, M Tl $\leqslant 10^{-6}$) erratic and irreproducible adsorption was observed both in column and shaking experiments. This erratic behavior may be caused by partial oxidation of Tl(I) to the strongly adsorbed Tl(III)[10b]; however, attempts to prevent adsorption of tracer Tl(I) by addition of ferrous or titanous chlorides as holding reductants were unsuccessful. In the presence of 1 M HF no significant adsorption was found in the range 0.1 to 11 M HCl in column experiments with *ca.* 10^{-3} M Tl(I) solutions.

The earlier adsorption data of Tl(III)[10b] in HCl have been reconfirmed, and are plotted in Fig. 3. Distribution coefficients decrease from *ca.* 3×10^5 near 1 M HCl to *ca.* 10^3 in 9 M HCl. Between 1 and 0.1 M HCl, D decreases slightly with decreasing HCl concentration. In the presence of 1 M HF the distribution coefficients of Tl(III) are slightly lower than in HCl alone and the two curves parallel each other closely.

1.11. **Germanium** (**Fig. 4**).—Adsorption of Ge(IV) becomes significant for M HCl > 4. The distribution coefficients rise with increasing M HCl to $D \approx 200$ in 10 M HCl.[10d,14] Measurements at high HCl concentrations are complicated by the volatility of $GeCl_4$. Addition of 1 M HF causes a marked change in the adsorption function and drastically decreases the volatility of Ge(IV) at high M HCl. In 1 M HF, D is less than unity for M HCl > 4. At lower HCl concentrations, D increases rapidly with decreasing M HCl to values in excess of 100 in 0.1 M HCl. Even larger values of D have been reported[15] for Ge(IV) in 1 M HF solutions (no HCl) with a similar resin in the fluoride form.

1.12. **Tin** (**Fig. 4**).—Adsorbability of Sn(II) is high throughout the region of HCl concentration studied. Adsorbability increases from $D = 500$ near 0.1 M HCl to a maximum $D = 10^3$ near 1 M HCl and then decreases with increasing HCl concentration to $D \approx 10$ in 12 M HCl. In the presence of 1 M HF adsorbability of Sn(II) is low in dilute HCl ($D = 4.4$ in 0.1 M HCl–1 M HF), increases with increasing HCl concentration to a maximum $D \approx 50$ near 2 M HCl, then decreases to $D \approx 10$ in 11 M HCl where the HCl–HF and the HCl adsorption functions have essentially merged.

Sn(IV) is strongly adsorbed from HCl solutions.[10e,16] Adsorbability increases from $D \approx 200$ near 0.5 M HCl to a broad maximum ($D \approx 10^4$) near 5 M HCl beyond which it decreases to $D \approx 6 \times 10^3$ in 12 M HCl. Adsorption of Sn(IV) was not studied below 0.5 M HCl, since precipitates formed in the Sn(IV) stock solutions on aging.

In HCl solutions containing 1 M HF no hydrolytic precipitation was observed even in dilute HCl solutions. In HCl–1 M HF the adsorption behavior of Sn(IV) markedly differs from that in HCl solutions: adsorption decreases from $D = 800$ in 0.1 M HCl to a minimum $D = 23$ near 1.5 M HCl; it then increases with increasing M HCl to $D = 3 \times 10^3$ near 11 M HCl where the HCl–HF function merges with the adsorption function for HCl.

Since adsorption of Sn(IV) is relatively high in all these HCl and HCl–1 M HF solutions, a few experiments were carried out at higher HF con-

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(13) R. A. Horne, *J. Inorg. Nuclear Chem.*, **6**, 338 (1958).

(14) See also Y. Yoshino, *Bull. Chem. Soc. Japan*, **29**, 78 (1956).

(15) U. Schindewolf and J. W. Irving, Jr., *Anal. Chem.*, **30**, 906 (1958).

(16) Y. Sasaki, *Bull. Chem. Soc. Japan*, **28**, No. 8, 614 (1956).

centrations in an attempt to find conditions where rapid elution would be feasible. While conditions were not found for very rapid elution ($D_v \leqslant 1$), satisfactory elution may be achieved with 2 M HCl–3 M HF ($D_v \approx 5$).

1.13. **Lead** (**Fig. 4**).—Adsorbability of Pb(II) increases with increasing M HCl from $D = 1$ in 0.05 M HCl to a maximum $D = 25$ near 1.5 M HCl beyond which it decreases to $D < 1$ for M HCl > 8.[10c] Except for a slight general lowering of distribution coefficients, 1 M HF has no effect on the adsorbability of Pb(II).

1.14. **Arsenic** (**Fig. 5**).—Adsorbability of As(III) from HCl solutions is negligible in the region $0.1 \leqslant M$ HCl < 4; for M HCl > 4 adsorbability rises to $D \approx 26$ in 11 M HCl.[10d,14] Arsenic(V) is but slightly adsorbed in the range $0.1 \leqslant M$ HCl $\leqslant 10$; distribution coefficients range from $D \approx 1.8$ in 0.1 M HCl to $D \approx 4$ near 10 M HCl. Presence of 1 M HF does not appreciably affect the adsorption functions of either As(III) or As(V).

1.15. **Antimony** (**Fig. 5**).—Distribution coefficients of Sb(III) are large throughout the HCl concentration range studied and increase from $D \approx 80$ in 0.1 M HCl to a maximum $D \approx 2 \times 10^3$ near 2 M HCl beyond which adsorbability decreases with increasing M HCl to $D \approx 50$ near 12 M HCl. Presence of 1 M HF markedly affects adsorbability of Sb(III). Thus, $D \approx 10$ for 0.1 M HCl–1 M HF; at higher HCl concentrations D decreases to a minimum ($D \approx 4$) near 2 M HCl–1 M HF and then rises to $D \approx 50$ near 11 M HCl–1 M HF.

Adsorption of Sb(V) becomes significant near 1 M HCl ($D \approx 1$) and rises with increasing M HCl to a broad maximum near 10 M HCl where $D \approx 2.5 \times 10^5$. Below 0.5 M HCl results were erratic possibly because of hydrolytic difficulties. Presence of 1 M HF markedly affects the adsorption function of Sb(V). Distribution coefficients are high in dilute HCl solutions ($D = 2 \times 10^3$ in 0.1 M HCl–1 M HF), they then decrease to a shallow minimum near 2.5 M HCl ($D \approx 3 \times 10^2$) beyond which they increase sharply to $D \approx 6 \times 10^4$ in 9 M HCl.

From inspection of the adsorption functions, Fig. 5, one might conclude that anion-exchange purification of Sb(V) could be carried out readily by first adsorbing it from concentrated HCl or from various HCl–HF mixtures and then eluting it with *ca.* 1 M HCl where adsorbability is low. To be sure, Sb(V) in 1 or 2 M HCl can be moved through columns without difficulty as expected from the equilibrium distribution coefficients. However, it has been our experience that once Sb(V) has been adsorbed it cannot be eluted readily, even with 1 M HCl from which, at equilibrium, it is not significantly adsorbed. Similar observations were reported by Sasaki[16] who believed that the difficulties resulted from reduction (on the resin) of Sb(V) to Sb(III) which is strongly adsorbed even in dilute HCl solutions. Sasaki further reported that Sb(V) can be eluted with 3 M HCl solutions if the element was introduced in this medium, if the resin had been pretreated with bromine and if the time elapsed between adsorption and elution was short. We have been unable to effect rapid removal of Sb(V) from bromine pretreated columns with 1 to 3 M HCl even if Sb(V) had been adsorbed from a strongly oxidizing medium such as 10 M HCl containing chlorine. We thus prefer to ascribe the difficulties to slow rates of interconversion of the various complexes, a phenomenon which frequently has been reported for Sb(V) in chloride solutions.[17]

1.16. **Bismuth** (**Fig. 5**).—Bi(III) is strongly adsorbed from HCl solutions. Adsorbability decreases from $D = 2 \times 10^5$ near 0.25 M HCl to $D = 57$ in 12 M HCl. The adsorption function of Bi(III) is not greatly altered by presence of HF except in the most dilute HCl solutions. Neither in HCl nor in HCl–HF medium is adsorption of Bi(III) sufficiently low to permit rapid elution. However, in the less acidic medium, 1 M NH_4Cl–1 M NH_4F, satisfactory elution of Bi(III) was observed. In this medium, Bi(III) apparently exists principally in the form of fluoride complexes which are not significantly adsorbed under these conditions.

2. **Separations.**—The adsorption functions of elements, as we have repeatedly mentioned, may be used directly to establish separation procedures. Indeed, the volume distribution coefficients D_v give, after correction for interstitial volumes, the number of column volumes necessary to obtain the element in maximum concentration (elution maximum) in the effluent. The criteria for satisfactory separations are (a) large ratios of the distribution coefficients of the ions to be separated and (b) low distribution coefficients (preferably $D_v \leqslant 1$) for the element to be eluted. With HCl as well as HCl–HF media diffusion in the resin is reasonably fast and serious difficulties in devising separations from inspection of distribution functions occur only when the rate of interconversion of the complexes is slow, as, for example, mentioned in Section 1.15 for Sb(V).

Since the anion exchange–HCl system has proven extremely useful for separations, one might wonder under what conditions it may be more advantageous to use the HCl–HF system. No doubt, HCl–HF systems are most useful in handling those elements of the 4th and 5th groups which in the absence of strong complexing agents tend to undergo hydrolytic reactions or are insoluble. For many of these elements, fluoride media permit handling in an easily reversible manner.

HCl–HF systems also are attractive media for separations involving those elements which in the presence of HF, at low HCl concentration, show increasing adsorption with decreasing HCl concentration. Some of these elements (*e.g.*, (Be(II)) do not adsorb significantly from HCl solutions and addition of HF represents a relatively simple change in medium to effect adsorption, compared with *e.g.*, use of organic ligands, which are often adsorbed by the resin, require careful *p*H and ionic strength control and are difficult to remove later.

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[17] See *e.g.*, (a) J. Whitney and N. Davidson, This Journal, **69**, 2076 (1947); **71**, 3809 (1949); (b) H. M. Neumann, *ibid.*, **76**, 2611 (1954); (c) H. M. Neumann and R. W. Ramette, *ibid.*, **78**, 1848 (1956).

In general this adsorbability in HF at low HCl concentrations provides a new set of conditions which can be exploited for separations, particularly since some elements, such as iron, do not show this type of adsorption.

At high HCl concentrations (no HF) Fe(III) is strongly adsorbed and can be isolated from the "non-adsorbable" elements; at low HCl concentrations where Fe(III) is not adsorbed it may be removed from another large group of elements which remain strongly adsorbed under these conditions. Utilizing HCl–HF media the number of elements from which iron readily can be removed is greatly expanded.[4c,5a] One may now take advantage of the fact that HF has little effect on the adsorbability of Fe(III) at high HCl concentrations, shows rapidly decreasing distribution coefficients with decreasing *M* HCl and remains non-adsorbable even at very low HCl concentrations.

A few elements are strongly adsorbed from chloride solutions and addition of HF sufficiently decreases adsorbabilities to permit their removal from columns within a reasonable number of column volumes of eluent. This is well demonstrated for Sn(IV) and Sb(III).

For some elements fluoride complexing in HCl–HF media is not sufficiently extensive to achieve low adsorbability but it may be reached in low acidity-fluoride solutions where complexing is greatly enhanced. In these cases it is also desirable to operate at high ionic strength where the negatively charged fluoride complexes are not strongly adsorbed. This device has been used successfully in separations involving Ta(V)[4b] and in the present paper it has been adapted to separations involving Bi(III).

In "neutral" fluoride solutions, of course, many more elements may exhibit extensive fluoride complexing than in HCl–HF solutions. Exploitation of these complexes for anion-exchange separations might become a fruitful field of study.[18] Unfortunately, in the low acidity-fluoride systems many more elements become insoluble than in the acid systems, thus limiting the broad applicability of this method. From the point of view of separations one might mention one additional advantage of the HCl–HF over the simple fluoride system: In view of the low selectivity of the exchangers for fluoride compared with chloride ions[19] the resin in HCl–HF mixtures remains almost completely in the chloride form making it possible to switch quickly from the HCl to the HCl–HF system without the delay incurred in changing resin forms. Nevertheless, *ca.* 1 column volume of eluent is required for resin equilibration since resin invasion by HF is by no means negligible.

The main disadvantages in using HF-containing systems for separations are the insolubilities of some elements (*e.g.*, some alkaline earths, rare earths) and the corrosive nature of the medium. The latter, on a laboratory scale, does not appear to be a serious handicap since suitable plastic equipment is now readily available or can be made in the laboratory. The insolubility of some elements is a more serious difficulty. If they are present in solution they must in general be separated ahead of the ion-exchange procedure since only at extremely low concentrations do they not introduce serious difficulties in the separations schemes.

Although many separations have been previously illustrated in HCl–HF media[3b,4,5] we felt it desirable to describe a few more typical cases involving elements more recently studied, in the hope that in this way HCl–HF solutions would become more widely recognized as suitable media for separations.

2.1. Separation of Be(II) and Al(III).—Be(II) is not sufficiently strongly adsorbed from HCl solutions to permit its separation from the large number of elements which are non-adsorbable in this medium. However in the presence of fluoride, at low HCl concentrations, Be(II) is significantly adsorbed and hence can be removed from many of these elements. A typical example is separation of Be(II) from Al(III), illustrated in Fig. 6. A small aliquot containing Be(II) (Be^7) and 10^{-3} *M* Al(III) in 0.01 *M* HCl–1 *M* HF was added to a 0.25 cm.^{2} × 4 cm. column which had been pretreated with the same HCl–HF solution. On elution with the same solution, Al(III) appears as a sharp band within the first column volume of effluent, while Be(II) remains on the column. Its removal can be effected with 1 *M* HCl.

2.2 Separation of Ti(IV) from V(IV).—This separation could be carried out in HCl solutions since at high HCl concentrations Ti(IV) is strongly adsorbed by anion exchangers, while V(IV) is not. However, even in concentrated HCl, Ti(IV) tends to precipitate. Further, dissolution of samples containing titanium is often difficult in the absence of strong complexing agents such as HF. These difficulties may be circumvented by use of HCl–HF media and excellent separations may be achieved as illustrated in Fig. 7A. A small aliquot containing 10^{-3} *M* Ti(IV) and V(IV) tracer (V^{48}) in 0.1 *M* HCl–1 *M* HF was added to a 0.25 cm.^{2} × 4 cm. column which had been pretreated with the same HCl–HF mixture. On elution, V(IV) appears as a sharp band within the first column volume of effluent, while Ti(IV) remains on the column, presumably as a fluoride complex. Ti(IV) can be removed with more concentrated HCl solutions containing HF; in the example 6 *M* HCl–1 *M* HF was used.

It appears worth re-emphasizing that with cation exchangers similar separations can often be achieved, though with elution order reversed. For this reason, the example Fig. 7B has been included. A solution containing 0.1 *M* Ti(IV), tracer V(IV) (V^{48}) and 0.1 *M* HCl–1 *M* HF was added to a cation-exchange column (Dowex-50 × 10). Vanadium(IV) is adsorbed, while Ti(IV) passes through the column, presumably because in this solution it exists principally as a negatively charged fluoride complex. Elution of V(IV) can be effected by displacement with hydrogen ions (*e.g.*, 1.5 *M* HCl). Since Ti(IV) is not adsorbed, this cation exchange method is particularly suited to separation of trace amounts of vanadium from large amounts of titanium. A typical application is the isolation of vanadium tracer (V^{48}) from ti-

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[18] See *e.g.*, ref. 15.

[19] R. M. Wheaton and W. C. Bauman. *Ind. Eng. Chem.*, **43**, 1088 (1951).

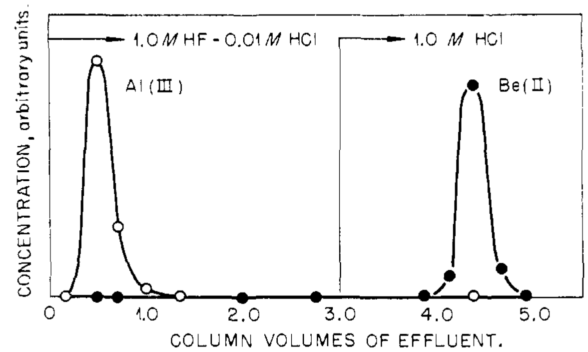

Fig. 6.—Separation of Al(III) and Be(II) by anion exchange.

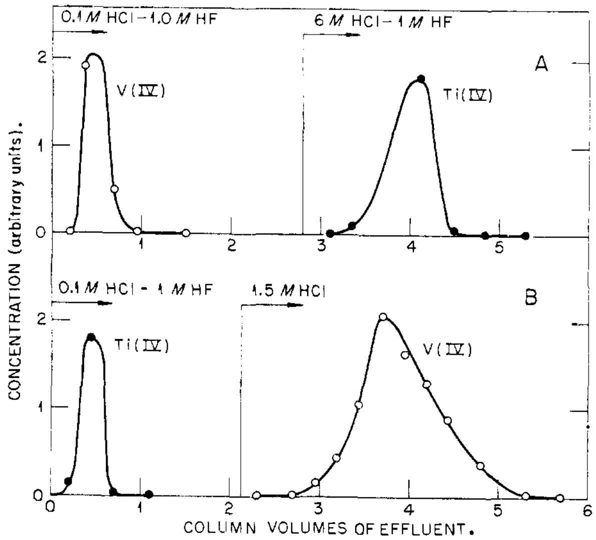

Fig. 7.—Separation of Ti(IV) and V(IV): A, anion exchange; B, cation exchange.

tanium cyclotron targets (see Experimental section).

2.3. Separation of Zn(II), Ga(III), Ge(IV) and As(V).—This separation can be achieved readily in HCl solutions because of the widely differing adsorbabilities of these elements. For example, if the sample were added in concentrated HCl solution to an anion-exchange column, As(V) would pass through, while Zn(II), Ga(III) and Ge(IV) are adsorbed. Germanium(IV) then can be eluted at an intermediate HCl concentration (*e.g.*, 5 *M*) where Zn(II) and Ga(III) remain adsorbed. Further decrease of *M* HCl, *e.g.*, to 1 *M*, would selectively remove Ga(III); Zn(II) finally could be removed from the column with very dilute HCl ($\leqslant 0.01$ *M*).

Unfortunately, Ge(IV) is very volatile at those HCl concentrations where it can be strongly adsorbed by the exchanger. Utilization of HCl–HF mixtures circumvents this difficulty and satisfactory sequential separation may be achieved, as illustrated in Fig. 8. An aliquot of a solution containing the appropriate tracers of these elements in 0.3 *M* HCl–1 *M* HF was treated with chlorine to ensure oxidation of arsenic to As(V) and added to a small resin column (0.25 cm.^{2} × 4 cm.) which had been pretreated with 0.3 *M* HCl–1 *M* HF containing chlorine. On elution with the same solution, Ga(III) appeared in a sharp band with peak concentration near 0.5 column volume. As(V) was removed on continued elution, as a sharp band with maximum concentration near 2.4 column volumes, well separated from Ga(III). Zn(II) was removed with 0.01 *M* HCl–1 *M* HF and, finally, Ge(IV) with 6 *M* HCl–1 *M* HF.

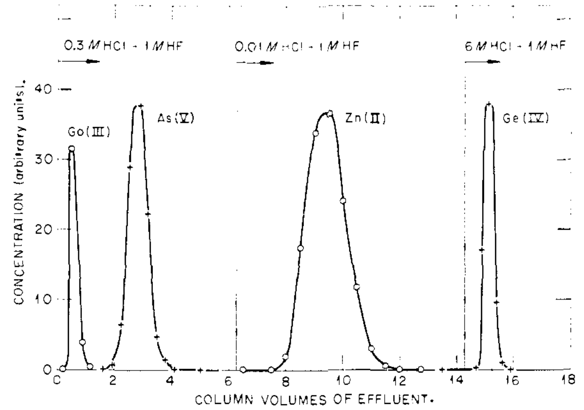

Fig. 8.—Separation of Zn(II), Ga(III), Ge(IV) and As(V) by anion exchange.

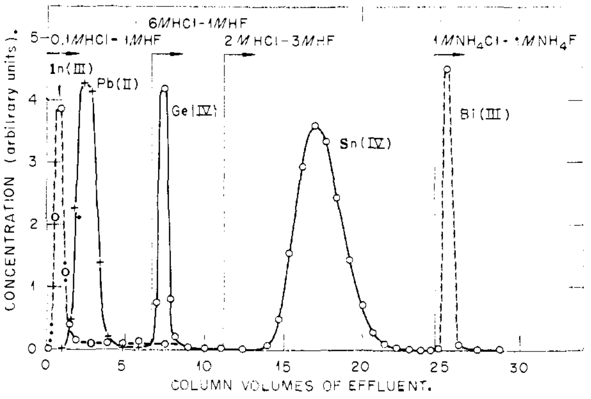

Fig. 9.—Separation of In(III), Pb(II), Ge(IV), Sn(IV) and Bi(III) by anion exchange.

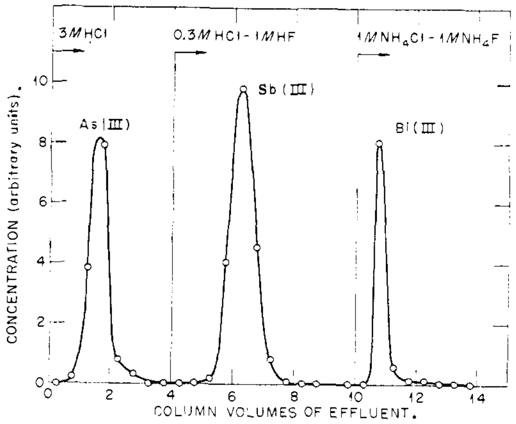

Fig. 10.—Separation of As(III), Sb(III) and Bi(III) by anion exchange.

2.4. Separation of Pb(II), In(III), Bi(III), Ge(IV) and Sn(IV).—The main purpose of this example is to illustrate the usefulness of fluoride containing media in the handling of tin and bismuth, elements which in HCl solutions (without

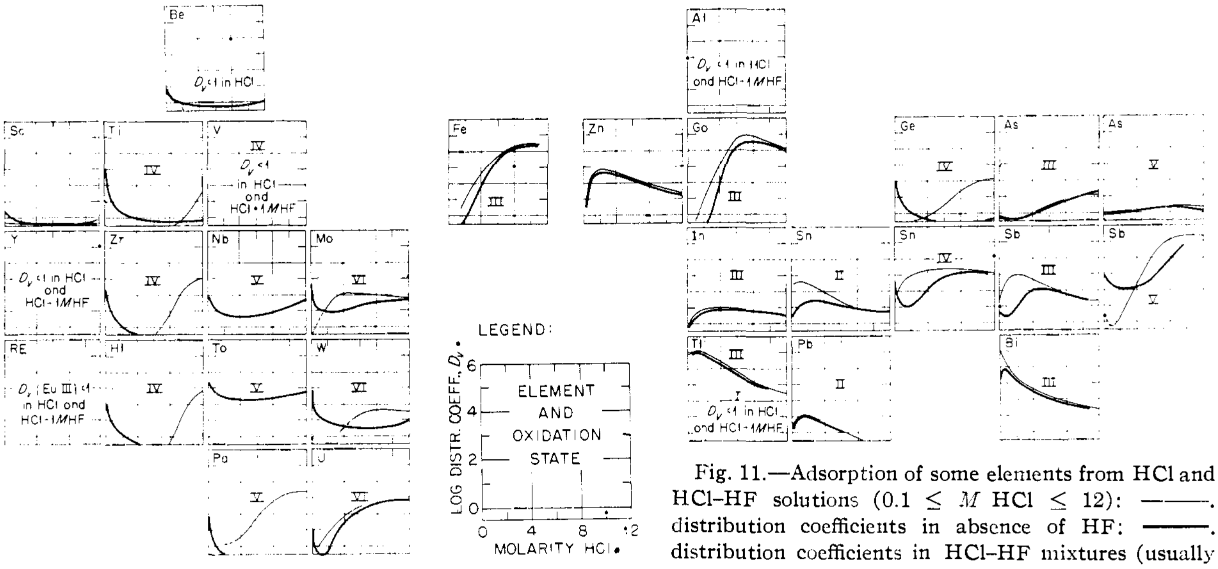

Fig. 11.—Adsorption of some elements from HCl and HCl-HF solutions ($0.1 \leq M$ HCl ≤ 12): ———. distribution coefficients in absence of HF: ———. distribution coefficients in HCl-HF mixtures (usually 1 *M* HF except Zr(IV), Hf(IV), Nb(V), Ta(V) and Pa(V) where *M* HF = 0.5).

fluoride) are adsorbed too strongly to permit elution within a reasonable number of column volumes. Actually, HCl-1 *M* HF solutions are also not satisfactory media for their rapid elution and for the separation illustrated in Fig. 9, other fluoride containing media were chosen.

The separation was carried out with 0.01 *M* Ge(IV) (Ge^{77}), 0.01 *M* Sn(IV) (Sn^{113}) and tracer Pb(II) (Pb^{210}, RaD). The daughter activities, In^{113m} and Bi^{210} (RaE) were also present and their elution bands are indicated by dashed lines in Fig. 9. A mixture of these elements in 0.1 *M* HCl-1 *M* HF was added to a 0.25 cm.^{2} × 4 cm. resin column. On elution with the same acid solution, In(III) appeared in a sharp band, followed by Pb(II) (elution maximum near 2.4 column volumes). Figure 9 shows trailing of the In(III) band, a consequence of the fact that the In(III) tracer, In^{113m} ($T_{1/2}$ = 1.75 hr.) is continuously being produced from the parent activity Sn^{113} still adsorbed on the resin. After removal of Pb(II), Ge(IV) was eluted in a sharp band with 6 *M* HCl-1 *M* HF. The Ge(IV) band was not appreciably contaminated with In^{113m} since In(III) is adsorbed from 6 *M* HCl-1 *M* HF. For elution of Sn(IV), 2 *M* HCl-3 *M* HF was chosen. In this medium Sn(IV) is still significantly adsorbed and a relatively broad, though symmetrical, elution band is obtained. Bismuth(III) could not be removed with HCl-HF solutions but satisfactory elution in a narrow band was achieved in a less acidic medium at moderately high ionic strength (1 *M* NH_4Cl-1 *M* NH_4F).

2.5. Separation of As(III), Sb(III) and Bi(III).—It is the purpose of this example (Fig. 10) to demonstrate that HCl-HF mixtures are satisfactory media for handling antimony in a reproducible manner. A small aliquot containing 0.01 *M* As(III) (As^{77}), 0.1 *M* Sb(III) (Sb^{124}) and Bi^{207} tracer in 9 *M* HCl was treated with a small amount of HBr (to prevent oxidation of As(III) to As(V)) and added to a small column (0.25 cm.^{2} × 4 cm.), pretreated with 3 *M* HCl. On elution with 3 *M* HCl, As(III) appeared in the effluent in a sharp band; Sb(III) was eluted with 0.3 *M* HCl-1 *M* HF and Bi(III) was removed, as in Sec. 3.4, with 1 *M* NH_4Cl-1 *M* NH_4F.

3. General Discussion.—As mentioned, the present studies were intended to supplement and expand our earlier studies of HCl-HF media. With the nineteen elements discussed here, the studies now cover, at least in a cursory manner, twenty-six elements including most of those metallic elements which in the presence of significant amounts of HCl might show substantial complexing by fluoride ions.

For ready comparison the adsorption functions of the elements studied by us in HCl-HF media are summarized as a series of plots of log D_v *vs.* *M* HCl at constant HF concentration (Fig. 11). Most of the data refer to 1 *M* HF solutions. For some of the metals studied earlier (Zr(IV), Hf(IV), Nb(V), Ta(V), Pa(V)) insufficient data were available for this medium and the adsorption functions plotted refer to 0.5 *M* HF solutions. Figure 11 also shows corresponding data for HCl solutions (thin lines) which were obtained with the same batch of resin. Comparative data were not included for Nb(V) and Ta(V) in HCl solutions since, in view of probable hydrolytic difficulties, the distribution coefficients are not considered sufficiently firmly established.

Before discussing in more detail the elements summarized in Fig. 11 it is desirable to consider briefly some of the elements not shown in this figure. There is little doubt that the alkali metals, which are non-adsorbable from HCl solutions, also are non-adsorbable in the presence of HF. The same should be true for the alkaline earths, provided difficulties from their low solubilities are avoided. The trivalent rare earths, such as Eu(III), except for solubility difficulties, should not be adsorbable from HCl-HF solutions, since, as indicated by their continued insolubility at high HF concentrations, they apparently do not form negatively charged complexes.

The divalent transition elements of the first row of the periodic table form very weak fluoride complexes[20] and, as confirmed by our studies with Zn(II), their adsorption functions in HCl and HCl–HF media should be substantially the same. The elements in the center of the second and third long rows of the periodic table (Ru to Cd, Os to Hg) form very strong chloride complexes and presumably much weaker fluoride complexes. In the presence of significant amounts of chloride ions, HF is thus not expected to affect appreciably their adsorbabilities. The same is probably also the case for Tc and Re, at least in their higher oxidation states where they normally exist as oxygenated anions in aqueous solutions.

Since, according to our data, In(III), Tl(III) and Pb(II) also have the same adsorption functions in HCl and HCl–HF it appears that the adsorbability in HCl of the large block of elements beyond subgroup VI (Cr) to the diagonal Ga, Sn, Bi are, with the exception of Fe(III), not affected by reasonable amounts of HF. Interestingly, the adsorption functions in HCl of As(III) and As(V) also are not affected by HF. This implies that arsenic acid does not react with HF in acid solution and that arsenic(III) is not sufficiently strongly complexed by fluoride ions to cause decomposition of the chloride complexes presumably formed at high HCl concentrations.

The large number of elements whose adsorption functions in HCl and HCl–HF differ significantly may qualitatively be divided into three groups:

(1) Elements whose adsorption functions merge at high HCl concentration and show increasing divergence at low HCl concentrations. For these elements the divergence can be correlated with the extent of formation of fluoride complexes; they apparently do not form negatively charged fluoride complexes in strongly acidic solutions. Typical examples are Fe(III), Ga(III), Sn(II).

(2) Elements whose adsorption functions merge at high *M* HCl, show substantial divergence at lower *M* HCl, and at still lower *M* HCl show increasing adsorption in the presence of HF. For these elements the divergence at high *M* HCl again reveals complexing by fluoride ions; the adsorption at low *M* HCl must be due to adsorption of negatively charged fluoride complexes. Typical examples are Sb(III), Sn(IV), Mo(VI), U(VI).

(3) Elements whose adsorption functions in HCl–HF are much lower than in HCl alone, particularly at high HCl concentrations: these elements are obviously extensively complexed by fluoride ions; most of them show the effect of negative complex formation as a rising adsorption function at low *M* HCl. Typical examples are Ti(IV), Zr(IV), Hf(IV), Ge(IV), Pa(V).

The anion-exchange data of the type presented, in principle permit quantitative conclusions regarding complex formation. Thus the shape of the adsorption functions at constant *M* HF and low *M* HCl should yield information regarding the average charge of the complexes.[2a] Present data are not sufficiently extensive to warrant this type of analysis. More fruitful appears brief consideration of the divergence of the HCl and HCl–HF adsorption functions at high *M* HCl.

Under conditions where the fluoride containing complexes are not significantly adsorbed compared with the chloride complexes one may estimate the fraction F' of the metal existing as fluoride containing complexes by the relationship

$$F' = 1 - D_{\mathrm{F}}/(D_{\mathrm{Cl}}R) \qquad (1)$$

Here D_{Cl} is the distribution coefficient in HCl solutions and D_{F} is its value in HCl–HF mixtures of the same HCl concentration. Equation 1 was originally presented[5a] without the factor R (*i.e.*, with $R = 1$) which is equivalent to the assumption that the activity coefficient quotients for the ion-exchange equilibria and the extent of resin invasion by chloride ions are independent of HF concentration. Present work shows that for systems in which complexing by fluoride ions seems negligible, the adsorption functions in HCl and HCl–HF are not superimposable but slightly displaced from each other. From the average displacement of the HCl and HCl–HF adsorption functions one may estimate $\log R = ca. -0.2$.[21]

TABLE I

COMPLEXING OF VARIOUS METALS BY FLUORIDE IONS IN HCl SOLUTIONS (1 *M* HF)

Element	Fraction of element as fluoride complexes in *M* HCl						
	0.5	1	2	4	6	8	11
Sn(II)	0.98	0.96	0.9	0.7	0.2	N[a] →	→
Fe(III)	←	> .98	.98	.8	.1	N →	→
Ga(III)	←	> .98	.98	.9	.5	0.3	N
Sb(III)	←	(−)[b]	> .99	.7	N →	→	→
Ti(IV)	←	←	(−)	←	←	←	>0.97
Zr(IV)	←	←	(−)	←	←	←	> .999
Hf(IV)	←	←	(−)	←	←	←	> .999
Ge(IV)	←	←	(−)	←	←	←	> .994
Sn(IV)	←	←	(−)	0.9	0.5	0.1	N
U(IV)				←	←	>0.99	
Pa(V)	←	←	(−)	←	←	←	>0.999
Sb(V)	←	←	(−)		0.95	0.9	
Mo(VI)	←	←	(−)	0.9	0.7	0.4	N
W(VI)	←	←	(−)	←	>0.9	0.8	0.6
U(VI)	←	(−)	>0.88	0.4	N →	→	→

[a] N, fraction of element as fluoride complexes negligible. [b] (−), evidence for predominance of negatively charged fluoride complexes.

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(20) See *e.g.*, J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part 2, Inorganic Ligands," The Chemical Society, London, Special Publication No. 7, 1958, pp. 88–93.

(21) If F' is determined as a function of HF (or F^-) concentration at constant *M* HCl one may compute complex constants for the equilibria involving fluoride ions. For example, let $k^{()}_{\mathrm{oi}} = (\mathrm{MCl}_i{}^{+z-i})/(\mathrm{M}^{+z})(\mathrm{Cl}^-)^i$ be the concentration quotients for the metal–chloride equilibria $\mathrm{M}^{+z} + i\mathrm{Cl}^- \rightarrow \mathrm{MCl}_i{}^{+z-i}$. Further, let $k^{()}_{\mathrm{oi(HF)}}$ be the concentration quotients for equilibria involving HF. For "pure" fluoride complexes $k_{\mathrm{oi(HF)}} = (\mathrm{MF}_i{}^{+z-i})(\mathrm{H}^+)^i/(\mathrm{M}^{+z})(\mathrm{HF})^i$ where, as in the expression for $k^{()}_{\mathrm{oi}}$, parentheses stand for concentration of species; for mixed fluoride–chloride complexes $k^{()}_{\mathrm{oi(HF)}}$ would also contain an appropriate power of the chloride concentration. Combining the expressions for $k^{()}_{\mathrm{oi}}$ and $k^{()}_{\mathrm{oi(HF)}}$ one obtains

$$\frac{1}{1 - F'} = 1 + \sum_{i=1}^{n'} k^{()}_{\mathrm{oi(HF)}} \frac{(\mathrm{HF})^i}{(\mathrm{H})^i} \Big/ \sum_{i=0}^{n} k_{\mathrm{oi}}{}^{()}(\mathrm{Cl})^i$$

Thus, only the ratios $k^{()}_{\mathrm{oi(HF)}} \Big/ \sum_{i=0}^{n} k^{()}_{\mathrm{oi}}(\mathrm{cl})^i$ are obtained from comparison of the adsorption functions in HCl and HCl–HF. Conversely, if chloride complexing is extensive $\left(\sum_{i=0}^{n} k^{()}_{\mathrm{oi}}(\mathrm{cl})^i \text{ large}\right)$, the adsorption functions for the two media may not differ greatly even if the element forms reasonably strong fluoride complexes.

As a first approximation R seems to be independent of HCl concentration and the same for all elements.

The extent of fluoride complexing was estimated for various metal systems according to eq. 1 with log $R = -0.2$ and the computed fractions F' are summarized in Table I. The values listed should be considered approximate though they are useful for demonstrating semi-quantitatively the wide differences in complexing properties of the elements. The method is of course adaptable to more precise determination of the extent of fluoride complexing though it requires more accurate measurement of D_F/D_{Cl} and of the factor R.

In the computation of F' according to eq. 1, adsorption of fluoride containing complexes is considered negligible. This seems to be the case for those elements which in HCl–HF are negligibly adsorbed at low HCl concentrations. For the other elements this condition is only met at very high HCl concentration.

Negatively charged fluoride complexes seem to be only moderately strongly adsorbed and their adsorption apparently becomes appreciable only at chloride concentrations less than *ca.* 3 M, where their presence is revealed by an increase of D_F with decreasing M HCl. In view of this low intrinsic adsorbability of negatively charged fluoride complexes, it is extremely difficult to establish their existence at high ionic strength. Thus even for the elements whose adsorbability in concentrated HCl essentially vanishes on addition of substantial amounts of HF, one can only conclude that they are essentially completely converted to fluoride complexes; a decision regarding the sign of the charge of these fluoride complexes at high M HCl must be deferred.

Acknowledgment.—We are indebted to Mrs. Donna Michelson and Dr. R. A. Day for permission to include some of their adsorption data for V(IV), Ti(IV) and Fe(III) in HCl–HF solutions.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, VICTORIA UNIVERSITY OF WELLINGTON]

The Composition of the Nitric Oxide Complexes of Cupric Halides[1]

BY R. T. M. FRASER[2] AND W. E. DASENT

RECEIVED JULY 31, 1959

The formation of a blue complex when nitric oxide is absorbed by solutions of cupric bromide or chloride is due to the presence of covalent molecules such as $CuBr_2 \cdot NO$. In ethanol, dissociation to colorless, ionic species takes place and these are shown to be responsible for erroneous reports of ion migration experiments. Reduction to cuprous bromide occurs upon reaction of nitric oxide with solutions containing less than two equivalents of bromide ion per cupric ion.

Absorption of nitric oxide by cupric salts in nonaqueous solvents with the simultaneous formation of deep blue solutions was first observed by Kohlschütter.[3] Several workers[4–8] have subsequently studied the complexes, but because the solid compounds have not been isolated from solution, and indeed are unstable even in solution, their composition and structure have usually been argued by analogy with the nitric oxide complexes of ferrous salt.[9]

The results of ion migration experiments[3] have been confusing and have led to the proposal of formulas such as $CuNo \cdot X_n^{(n-2)-}$, $CuX_2 \cdot NO$ and $Cu(EtOH)_3 \cdot NO^{++}$ (X = Br or Cl). Since the nitric oxide is coördinated in the +I state (as the nitrosonium ion),[8] the complexes are important because of their possible relationship to the carbon monoxide–cuprous chloride complex.

This study was undertaken to define the stoichiometry of the complexes and to reinterpret the ion migration experiments.

Experimental

Reagents.—All chemicals were of analytical reagent grade unless stated and were stored in sealed bottles in vacuum desiccators until required. Ethyl alcohol was refluxed over magnesium turnings in the presence of a trace of iodine to yield "super dry alcohol."[10] Acetonitrile was distilled twice and stored in a brown bottle away from light.[11] Formic acid was distilled and then fractionally crystallized.

Cupric bromide was prepared from cupric oxide and hydrobromic acid.[12] The brown crystals were dried in a desiccator, finely powdered, then returned to the desiccator for a week before use. Anhydrous cupric chloride was prepared from the hydrate by warming in a stream of dry hydrogen chloride.[12] The cupric salts were analyzed frequently; no change in the copper or halide content occurred during the course of experiments.

Nitric oxide was prepared from ferrous sulfate, sulfuric acid and sodium nitrite.[13] As evolution of gas was slow, powdered pumice or calcium sulfate was added to the mixture (1 g. to 25 ml. of solution). Calcium sulfate was the more efficient and evolution of gas was complete within one min.

Gas Absorption Measurements.—The nitric oxide was stored in a reservoir until needed, then slowly forced through scrubbers containing successively concentrated sodium hydroxide solution and concentrated sulfuric acid. The scrubbers were cleaned and refilled after every twenty absorption measurements. The gas then passed to a buret connected to a manometer and to the absorption flask. Before each measurement the absorption flask was carefully

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[1] From a dissertation submitted by R. T. M. Fraser in partial fulfillment of the requirements for the degree of Master of Science, Nov., 1957.

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