[Contribution from the Oak Ridge National Laboratory, Chemistry Division]

Anion-exchange Studies. XVII. Molybdenum(VI), Tungsten(VI) and Uranium(VI) in HCl and HCl–HF Solutions[1,2]

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The anion exchange behavior of Mo(VI), W(VI) and U(VI) was investigated with a strong base quaternary amine anion-exchange resin in HCl solutions and in HCl–HF mixtures. The elements adsorb strongly at high HCl concentrations. Adsorption decreases with decreasing *M* HCl and, except for W(VI) which tends to precipitate, becomes negligible near 0.5 *M* HCl. The adsorbabilities in HCl solutions containing 1 *M* HF differ widely and separation is readily achieved. A number of separations of these elements from each other and from other elements, particularly Fe(III), are illustrated. The effect of cross-linking on the separations is discussed.

In continuation of a systematic survey of the anion-exchange behavior of the metals in HCl solutions, the adsorbabilities of Mo(VI), W(VI) and U(VI) have been determined. Conditions were not found for the complete separation of these elements in this medium even with resins of different cross-linking. Studies in HCl–HF mixtures were carried out since, on the basis of earlier work with elements of the fourth and fifth groups,[3] considerably better separability may be achieved by the use of such mixed systems than with HCl alone.

Experimental

As in earlier work,[4] adsorbabilities were determined either by the column or by the equilibrium method, depending on the magnitude of the distribution coefficients D (amount per kg. dry resin/amount per liter of solution[5]). For low values of D the equilibrium method is less accurate than the column method, while the latter becomes relatively cumbersome when D becomes large. A shift from the one method to the other was made in the neighborhood of D = *ca.* 20. The column method readily yields[3a] a volume distribution coefficient D_v[6] which is related to D by the relationship $D_v = \rho D$, where ρ is the bed density. For present purposes $1/\rho = 2.2$ liters per kg. dry resin was taken.

Metal concentrations were determined radiometrically, using as tracers Mo^{99} (β, γ, $T_{1/2}$ = 67 hr.); W^{185} (β, γ, $T_{1/2}$ = 73 d.) and U^{233} (α, $T_{1/2} = 1.6 \times 10^5$ yr.).

The Mo^{99} tracer was prepared by neutron bombardment of reagent grade MoO_3 in the ORNL Low Intensity Training Reactor (LITR). The irradiated oxide was dissolved in 0.5 *M* NaOH and aliquots of this "stock" solution were used after acidification. Half-life determinations showed the tracer to be of satisfactory purity. Since the tracer contained the daughter activity Tc^{99} ($T_{1/2}$ = 6 hr.) final counting was done after secular equilibrium had been reached. By extrapolation of the counting data to "zero time" (time of separation of the phases) it was demonstrated that under all conditions studied technetium was more strongly adsorbed than molybdenum.

High specific activity W^{185} tracer was obtained[7] in 0.7 *M* KOH and portions of this "stock solution" were used after acidification. On the basis of a number of column experiments the tracer appeared to be essentially free of other activities. The U^{233} tracer was found by α-pulse analysis to contain less than 1% of non-uranium α-activity.[8]

The separations experiments were usually carried out with small columns (*ca.* 1 ml., 1 to 2 inches high). Small aliquots (*ca.* 0.5 cc.) of the test solutions were permitted to seep into the columns which had been pretreated with the same acids as used in the test solutions. The solutions usually contained the appropriate tracers to facilitate analysis. Metal concentrations varied from tracer levels to *ca.* 10^{-2} *M*, although higher concentrations could probably be used provided the columns are not overloaded. Flow rates in the separations were usually between 0.5 and 1 cm./min.

The experiments were carried out in an air-conditioned room at 25 ± 2°. For the experiments involving fluoride solutions, fluoride-resistant containers were used, *i.e.*, Lusteroid test-tubes, columns made of Tygon tubing with retaining plugs of lucite shavings, plastic burets and pipets. Except where otherwise noted, the same batch of quaternary amine polystyrene divinyl benzene resin (Dowex-1, 10% DVB, 200–230 mesh) was used as in the earlier work.[9] Further details of the experimental procedure will be given in the discussion of the various systems.

Results and Discussion

1. Mo(VI), W(VI) and U(VI) in HCl Solutions.—The results of the experiments are summarized in Fig. 1 as a plot of log D *vs.* *M* HCl, where D is the weight distribution coefficient (amount per kg. dry resin/amount per liter of solution).

The adsorbability of Mo(VI) is small in *ca.* 0.5 *M* HCl (D = *ca.* 2), rises rapidly to a maximum near 5 *M* HCl (D = *ca.* 250) and then slowly decreases with increasing *M* HCl. The reliability of the values of D at the highest and lowest HCl concentrations is somewhat in doubt. At high *M* HCl, Mo(VI) tends to precipitate while at very low *M* HCl (dashed line, Fig. 1) slow equilibria cause complications. Thus below 1 *M* HCl Mo(VI) tends to tail and elutes in the form of two bands which follow each other closely (*e.g.*, in 0.5 *M* HCl maxima appear at 1.4 and 2.4 column volumes). This implies that at least two species of Mo(VI) exist under these conditions, which are not in rapid equilibrium with each other, as might be expected from the rather complicated hydrolytic behavior of Mo(VI). When elution is carried out with 1 *M* HCl, Mo(VI) appears as a symmetrical band. Although D (see Fig. 1) is somewhat higher at this acidity than at lower HCl concentrations, removal seems to be optimal near 1 *M* HCl.

The adsorbability of W(VI) at HCl concentrations larger than 6 *M* first increases with *M* HCl

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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.

[2] Previous paper: F. Nelson and K. A. Kraus, This Journal, **77**, 1391 (1955).

[3] (a) K. A. Kraus and G. E. Moore, *ibid.*, **73**, 9 (1951); (b) **73**, 13 (1951); (c) **73**, 2900 (1951); (d) **77**, 1383 (1955).

[4] See, *e.g.*, K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

[5] Values of D were computed on the basis of weights of resin dried over Anhydrone in a vacuum desiccator at 60°. Metal concentrations were held sufficiently low to permit measurement of D at less than 1% loading of the resin.

[6] The volume distribution coefficient D_v can be calculated from the relationship $D_v = (V/Ad) - i$, where V is the volume at which the eluted ion appears in maximum concentration in the effluent, where A is the cross-sectional area, d the length of the column (*i.e.*, Ad is one column volume) and where i is the fractional interstitial space of the column. For present computations i = 0.42 was assumed.

[7] We are indebted to the ORNL Isotopes Division for the tracer.

[8] We are indebted to Mrs. Myrlene Davis of the ORNL Instruments Division for the α-spectrometer analyses.

[9] For characterization of the resin, see K. A. Kraus and G. E. Moore, This Journal, **75**, 1457 (1953).

and reaches a shallow maximum near 8 *M* HCl. For HCl concentration less than 6 *M*, *D* tends to decrease with decreasing *M* HCl. However, adsorption becomes markedly dependent on equilibration time and elution becomes unsatisfactory. Thus, if W(VI) is adsorbed at high HCl concentrations and the column treated with 1 to 3 *M* HCl, part of the W(VI) is removed within a few column volumes, though most of it remains on the column. This behavior at low *M* HCl is probably connected with the formation of hydrolytic polymers of W(VI) and their tendency to precipitate. Adsorbability of W(VI) is generally less than that of Mo(VI) and its adsorption maximum occurs at higher *M* HCl.

The adsorbability of U(VI) rises rapidly with increasing *M* HCl from essentially negligible values near 0.5 *M* HCl to a shallow maximum near 10 *M* HCl. Up to *ca.* 4 *M* HCl the values of *D* of Mo(VI) and U(VI) are very similar, although U(VI) at higher *M* HCl adsorbs considerably more strongly than Mo(VI).

2. Separations in HCl Media. Effect of Cross-linking.—The strong adsorbability of Mo(VI), W(VI) and U(VI) at high *M* HCl permits separation of these elements from the many elements which under these conditions show little adsorption. Advantage may also be taken of the low adsorbability of Mo(VI) and U(VI) at low *M* HCl to effect separations from elements which adsorb strongly under these conditions. Unfortunately, removal of W(VI) (and to some extent of Mo(VI)) from columns is complicated by its hydrolytic properties, as discussed in section 1. Furthermore, the similarity of the distribution functions of Mo(VI) and U(VI) at low *M* HCl makes their separation from each other difficult.

At high *M* HCl Mo(VI), W(VI) and U(VI) show considerable differences in adsorbability. However, these differences cannot be exploited for separations, since the values of *D* are too high. Since Herber and Irvine[10] recently showed that adsorbabilities of complex ions are greatly dependent on the cross-linking (% DVB) of the resin,[11] it appeared that at lower cross-linking than the present 10% DVB, the distribution coefficients at high *M* HCl might become sufficiently low for convenient separations. As shown in Table I, where the volume distribution coefficients D_v are listed, adsorption at 1% DVB appears to be sufficiently low to permit separation of W(VI) and U(VI), while the values of D_v for Mo(VI) and W(VI) at 1% DVB, though low, are not sufficiently different for convenient separation with short columns.

TABLE I

DEPENDENCE OF DISTRIBUTION COEFFICIENTS ON CROSS-LINKING

Element	HCl, *M*	Vol. distribution coefficient (D_v) 10% DVB	Vol. distribution coefficient (D_v) 1% DVB	$\frac{D_v\ (10\%\ \text{DVB})}{D_v\ (1\%\ \text{DVB})}$
Mo(VI)	12	64	6.5	10
W(VI)	12	33	4	8
U(VI)	12	712	19.5	37
U(VI)	3.05	42	1.8	23
Fe(III)	3.05	122	6.4	19

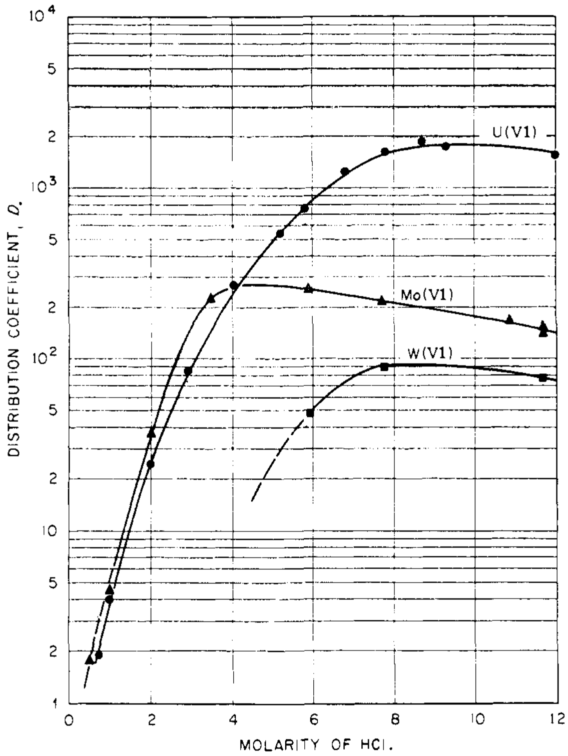

Fig. 1.—Adsorption of Mo(VI), W(VI) and U(VI) from HCl solutions.

Typical separations with this resin of low cross-linking are shown in Fig. 2. An aliquot of a solution containing W(VI) and U(VI) in 12 *M* HCl was added to a column of a low cross-linked resin (Dowex-1, 1% DVB, 50–100 mesh). Elution was carried out with 12 *M* HCl. With this relatively short column (5.8 cm.) separation was barely achieved (Fig. 2a). After removal of W(VI) more rapid elution, and hence a sharper elution band, of U(VI) could have been obtained with an HCl solution of lower concentration.

A separation of U(VI) from Fe(III) is shown in Fig. 2b. This separation is quite difficult with a highly cross-linked resin in HCl media since Fe(III) at high *M* HCl, where $D_{Fe(III)} >> D_{U(VI)}$, adsorbs very strongly[12] while at low *M* HCl where adsorption is low enough for convenient elution $D_{Fe(III)}$ differs only little from $D_{U(VI)}$. An aliquot of a solution containing Fe(III) and U(VI) in 5 *M* HCl was added to a column of the low cross-linked resin. On elution with 3 *M* HCl U(VI) appeared in the effluent with maximum concentration near 2.2 column volumes. It was reasonably free of Fe(III) which appeared in a broad band with maximum concentration near *ca.* 7 column volumes. As in the previous experiment a shift to lower *M*

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[10] R. Herber and J. W. Irvine, Jr. (private communication). We are indebted to Drs. Herber and Irvine for making this work available to us before publication.

[11] These observations are in qualitative agreement with earlier findings on the effect of cross-linking on adsorbability of simple ions, particularly cations on cation exchange resins. See *e.g.*, R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **43**, 1089 (1951); H. P. Gregor, THIS JOURNAL, **73**, 643 (1951); E. Glueckauf, *Proc. Roy. Soc.* (*London*), **214A**, 207 (1952); and K. W. Pepper and E. Reichenberg, *Z. Elektrochem.*, **57**, 183 (1953).

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

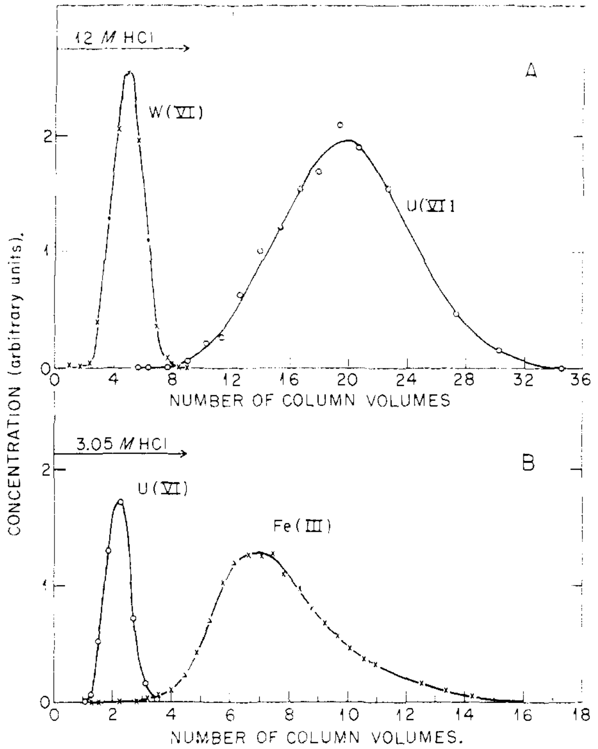

Fig. 2.—Separations with low cross-linked (1% DVB) resin.

HCl after removal of U(VI) would have eluted Fe(III) quicker and in a sharper band.

To summarize, by the use of resins of low cross-linkage distribution coefficients may be sufficiently lowered to permit some separations which cannot readily be achieved with a highly cross-linked resin. This effect is expected to be general.

3. Mo(VI), W(VI) and U(VI) in HCl–HF Mixtures.—A study of the adsorption behavior in HCl–HF mixtures appeared promising since, on the basis of earlier work with the elements of the fourth and fifth groups,[3] addition of fluoride was expected to affect greatly the adsorbabilities of these elements of the sixth group, magnify their differences, and avoid difficulties resulting from hydrolytic precipitation. A series of equilibration and column experiments was carried out in 1 *M* HF solutions as a function of *M* HCl. The results are summarized in Fig. 3.

The adsorbability of Mo(VI) is considerably decreased by the addition of 1 *M* HF to a minimum $D = 18$ near 2 *M* HCl. At lower *M* HCl the distribution coefficients of Mo(VI) rise rapidly with decreasing *M* HCl. A similar effect of HF is found for W(VI). An adsorption minimum for W(VI) occurs near 8 *M* HCl ($D = ca.\ 7$) where elution of W(VI) is practical, though not necessarily optimal. A search for optimum conditions ($D \leqslant 2$) would involve a more detailed study of the effect of HF concentration on adsorbabilities. The effect of HF on the adsorbability of U(VI) is relatively small at high *M* HCl but increases with decreasing *M* HCl. At HCl concentrations less than 1 *M*, *D* of U(VI) rises rapidly with decreasing *M* HCl. In this respect U(VI) is similar to Mo(VI) and W(VI), although the adsorbability of

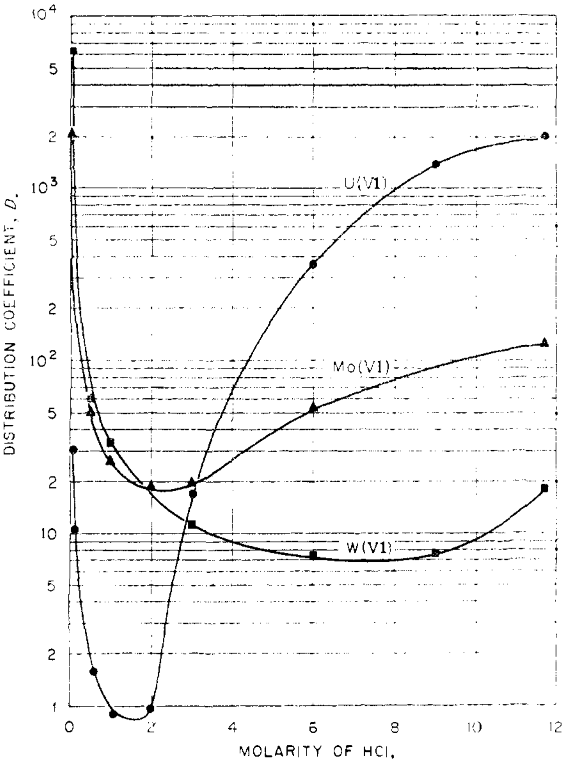

Fig. 3.—Adsorption of Mo(VI), W(VI) and U(VI) from HCl–HF solutions (1 *M* HF).

U(VI) at low *M* HCl in the presence of HF appears to be considerably less than that of the other two elements. The marked adsorption differences of these elements of the sixth group in HCl–HF mixtures permit satisfactory separation of these elements.

After this study had been completed, a publication by Hague, Brown and Bright[13] on the anion-exchange separation (Dowex-1) of Ti(IV), Nb(V), Mo(VI) and W(VI) in HCl–HF mixtures appeared. Our data in fluoride solutions are in good agreement with theirs in the HCl concentration range in which our studies overlap.

4. Separations in HCl–HF Mixtures. (a) Separation of Mo(VI), W(VI) and U(VI).—Inspection of Figs. 1 and 3 reveals that a variety of conditions can be selected for separations involving these elements. Two typical separations are demonstrated in Fig. 4. An aliquot of a solution containing W(VI) and U(VI) in 9 *M* HCl–1 *M* HF was added to a small column of the highly cross-linked resin. On elution with 9 *M* HCl–1 *M* HF (see Fig. 4a) W(VI) appeared in the effluent in a relatively sharp band within the first few column volumes. U(VI) remained strongly adsorbed on the column and was eluted with dilute HCl (0.1 *M*).

In Fig. 4b the separation of Mo(VI), W(VI) and U(VI) from each other is illustrated. Conditions were selected to reverse the elution order of W(VI) and U(VI). An aliquot of a solution containing these elements in 0.5 *M* HCl–1 *M* HF was added to a column. On elution with 0.5 *M* HCl–1 *M* HF, U(VI) appeared in the effluent in a narrow band

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[13] J. L. Hague, E. D. Brown and H. A. Bright, *J. Research Natl. Bur. Standards*, **53**, 261 (1954).

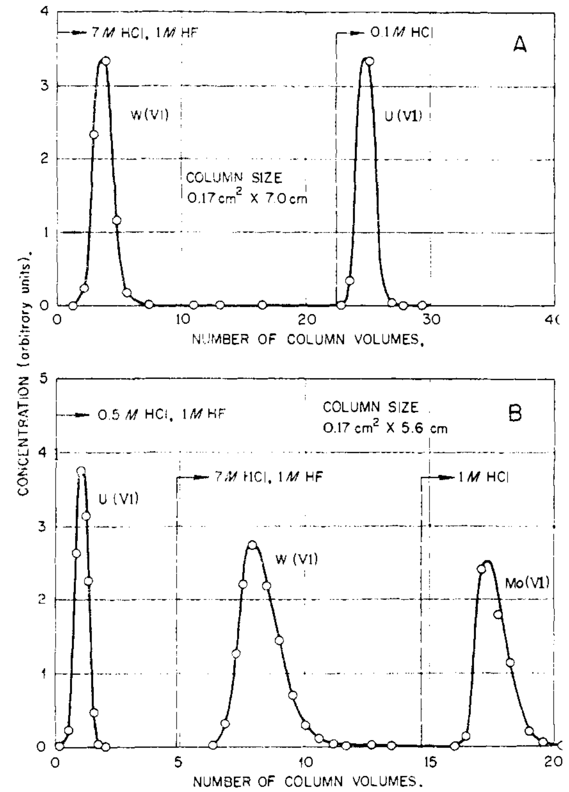

Fig. 4.—Separations involving Mo(VI), W(VI) and U(VI).

almost immediately, while Mo(VI) and W(VI) remained on the column. Removal of W(VI) was effected with 9 *M* HCl-1 *M* HF and removal of Mo(VI) with 1 *M* HCl. The Mo(VI) band tailed slightly, though not seriously.

The addition of fluoride in the beginning of a separation is often undesirable since some elements may be present which are precipitated by it (*e.g.*, alkaline earths or rare earths). However, adsorption of Mo(VI), W(VI) and U(VI) can be carried out from HCl solutions (*e.g.*, 9 *M* HCl) in the absence of fluoride and interfering ions washed out. W(VI) may then be eluted with 9 *M* HCl-1 *M* HF, U(VI) with 1 *M* HCl-1 *M* HF and Mo(VI) with 1 *M* HCl.

(b) **Separation of Fe(III) from Mo(VI), W(VI) and U(VI).**—In a series of equilibration experiments with Fe(III) (Fe^{59}) in 1 *M* HF solutions containing varying amounts of HCl, it was established that HF decreases $D_{\mathrm{Fe(III)}}$ though only slightly in concentrated HCl. The effect increases with decreasing *M* HCl in a manner similar to the effect of HF on $D_{\mathrm{U(VI)}}$. However, in contrast to the behavior of U(VI) (as well as Mo(VI) and W(VI)) $D_{\mathrm{Fe(III)}}$ in the presence of 1 *M* HF remains low, at least down to 10^{-2} *M* HCl.

For the separation of Fe(III) from W(VI) advantage may be taken of the high adsorbability of Fe(III) and the low adsorbability of W(VI) in 9 *M* HCl-1 *M* HF. If a 9 *M* HCl-1 *M* HF solution containing these elements is passed into a column and elution carried out with 9 *M* HCl-1 *M* HF, W(VI) can be removed while Fe(III) is adsorbed strongly. Removal of Fe(III) can be effected with HCl of low concentration, *e.g.*, 0.5 *M* HCl.

The separation of Fe(III) from Mo(VI) can similarly be achieved. For example, if a mixture of these elements in 9 *M* HCl is passed into a column, both elements are adsorbed while non-adsorbable elements pass through the column. Fe(III) may then be eluted with HCl-HF mixtures of low HCl concentration (*e.g.*, 0.01 *M* HCl-1 *M* HF) under conditions where Mo(VI) remains adsorbed. Mo(VI) may then be removed with *ca.* 1 *M* HCl in the absence of HF.

By combination and modification of these techniques Fe(III) can be removed from both Mo(VI) and W(VI) as illustrated in Figs. 5a and b. For the experiment described in Fig. 5a a small aliquot of a solution containing Fe(III), W(VI) and Mo(VI) in 0.5 *M* HCl-1 *M* HF was added to a column. On elution with 0.5 *M* HCl-1 *M* HF, Fe(III) practically immediately appeared in the effluent while Mo(VI) and W(VI) were retained by the column. W(VI) was removed with 9 *M* HCl-1 *M* HF and then Mo(VI) with 1 *M* HCl.

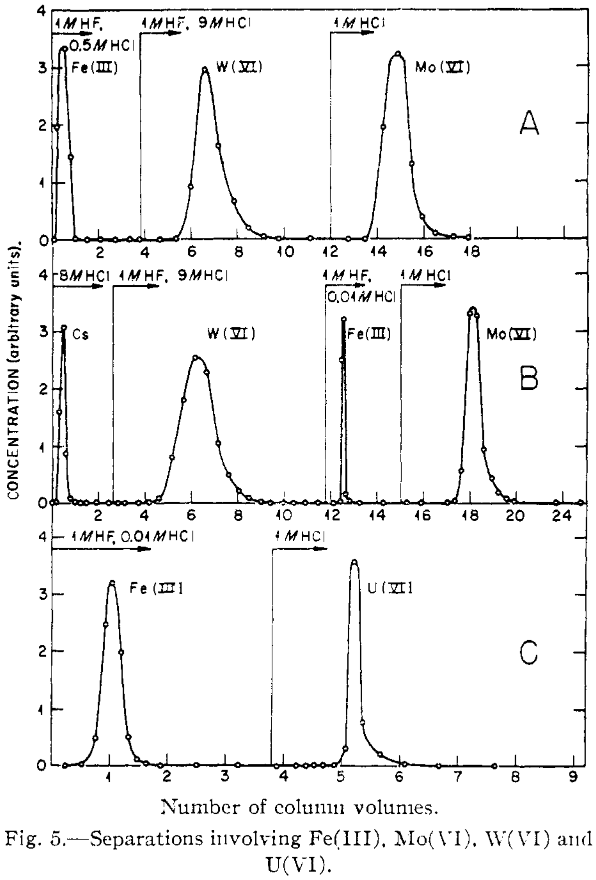

Fig. 5.—Separations involving Fe(III), Mo(VI), W(VI) and U(VI).

Conditions may also be chosen to reverse the order of elution of Fe(III) and W(VI) (Fig. 5b). An aliquot of a solution containing Mo(VI), W(VI), Fe(III) and Cs^{137} in 9 *M* HCl-1 *M* HF was added to a column. In this experiment Cs^{137} was added to demonstrate the behavior of a typical non-adsorbable element. On elution of the column with 9 *M* HCl-1 *M* HF, Cs^{137} and W(VI) appeared in separate bands with maximum concentrations at 0.4 and 3.7 column volumes, respectively. Mo(VI) and Fe(III) were retained by the column.

Removal of Fe(III) was achieved with 0.01 *M* HCl–1 *M* HF, and removal of Mo(VI) with 1 *M* HCl.

Separation of Fe(III) and U(VI), which is quite difficult at moderate HCl concentrations where these elements adsorb similarly even in the presence of HF, can be achieved readily at low HCl concentrations where U(VI) adsorbs strongly and Fe(III) shows only negligible adsorption. For the experiment described in Fig. 5c a small aliquot of a solution containing Fe(III) and U(VI) in 0.01 *M* HCl–1 *M* HF was passed into a column. Fe(III) was removed with 0.01 *M* HCl–1 *M* HF and then U(VI) with 1 *M* HCl.

The separation of Fe(III) from Mo(VI), W(VI) and U(VI) is also feasible at low HCl concentrations in 1 *M* HF where Fe(III) does not adsorb and these elements of the sixth group adsorb strongly. Unfortunately, however, the separation of these four elements from each other is difficult to achieve in one pass. It was hoped that one could adsorb these elements from concentrated HCl, remove W(VI) as in the experiment Fig. 5b with 9 *M* HCl–1 *M* HF, remove Fe(III) with 0.01 *M* HCl–1 *M* HF, but retain U(VI) on the column under these conditions. Although U(VI) adsorbs strongly from this last medium, desorption of U(VI) occurs while the column adjusts itself from 9 *M* HCl–1 *M* HF to 0.01 *M* HCl–1 *M* HF since between these extremes is a region of HCl concentrations where U(VI) shows negligible adsorption.

5. Some Considerations Regarding Species in Solution.—The great similarity of the distribution functions of Mo(VI) and U(VI) and particularly the similarities of the slopes d log D/d m_{HCl} at low *M* HCl suggest that the initial complexing reactions of these elements are similar and that the equilibrium constants for these chloride complex equilibria are approximately the same. This implies that the uncomplexed Mo(VI) species in the more acidic solutions (M HCl $\geqslant$ 1) is MoO_2^{++} in analogy with the uranyl ion UO_2^{++}. It has been known for some time that at acidities larger than *ca.* 0.1 *M* Mo(VI) exists in the form of positively charged ions, probably polymeric.[14] Recently it has been suggested from solubility measurements[14b] that positively charged polymeric Mo(VI) species occur at least up to *ca.* 1.2 *M* acid ($HClO_4$). With respect to formation of such polymeric cations Mo(VI) thus appears to be similar to U(VI)[15] although the region of polymer formation extends to considerably higher acidities for Mo(VI) than for U(VI). The slow anion exchange equilibria of Mo(VI) at low acidities are consistent with the postulated existence of polymeric species. It is tempting to conclude from the anion-exchange results that these polymers depolymerize to MoO_2^{++} (and its chloride complexes) at higher acidities, at least at the low Mo(VI) concentrations used in the equilibration experiments (*ca.* 10^{-4} *M*).

The uncomplexed species of W(VI) may also become monomeric WO_2^{++}, although only at much higher acidities than for Mo(VI). At acidities less than 6 *M* the anion-exchange results are consistent with the assumption that positively charged polymeric ions (which may slowly precipitate) predominate, even at the low W(VI) concentrations used here (10^{-4} *M* in the equilibration experiments).

At the present time relatively little can be stated definitely regarding the negatively charged chloride complexes which are formed by these elements. The complexes are probably of the type $MO_2Cl_n^{-n+2}$ and for the negatively charged complexes $n = 3$ or 4 is likely. If the position of the adsorption maxima is taken as an indication of the relative strength of the chloride complexes the order becomes Mo(VI) > W(VI) > U(VI).

Comparison of the distribution coefficients in HCl (D_{Cl}) and HCl–HF solutions (D_F) gives some information regarding the fraction of the metal in the form of fluoride complexes. Let m_t and m_t^r be the stoichiometric concentrations of the metal in the aqueous and resin phases, then the distribution coefficients can be expressed as

$$D_{Cl} = \frac{(m_t^r)_{Cl}}{(m_t)_{Cl}} \quad \text{and} \quad D_F = \frac{(m_t^r)_F}{(m_t)_F} \tag{1}$$

where subscripts Cl and F refer to the measurements in HCl and HCl–HF solutions, respectively. If we designate the concentration of species by parentheses, consider only monomeric species and sum over all species, the stoichiometric concentrations can be expressed as

$$(m_t)_{Cl} = \sum_{i=0}^{n} (MCl_i)_{Cl};$$

$$(m_t)_F = \sum_{i=0}^{n} (MCl_i)_F + \sum_{i=1}^{n'} (MF_i)_F \tag{2}$$

Combination of equations 1 and 2 yields

$$\frac{1}{D_F} - \frac{1}{D_{Cl}} = \frac{\Sigma(MCl_i)_F}{(m_t^r)_F} + \frac{\Sigma(MF_i)_F}{(m_t^r)_F} - \frac{\Sigma(MCl_i)_{Cl}}{(m_t^r)_{Cl}} \tag{3}$$

If D_F and D_{Cl} are obtained at the same chloride concentration, if m_t^r is small compared with the capacity (low loading, linear isotherm) and if the assumptions are made that only chloride complexes are adsorbed and that the activity coefficient ratios for the complex equilibria and resin equilibria are not affected by the presence of HF, then

$$\frac{\Sigma(MCl_i)_F}{(m_t^r)_F} = \frac{\Sigma(MCl_i)_{Cl}}{(m_t^r)_{Cl}} \tag{4}$$

Since furthermore

$$\frac{\Sigma(MF_i)_F}{(m_t^r)_F} = \frac{\Sigma(MF_i)_F(m_t)_F}{(m_t^r)_F(m_t)_F} = \frac{1}{D_F}\,\frac{\Sigma(MF_i)_F}{(m_t)_F} \tag{5}$$

equation (3) simplifies to

$$1 - \frac{D_F}{D_{Cl}} = \frac{\Sigma(MF_i)_F}{(m_t)_F} \tag{6}$$

which gives the fraction of the metal in the form of fluoride complexes ($\Sigma(MF_i)_F/(m_t)_F$) as a function of the ratio D_F/D_{Cl}. As mentioned, these computations are of course applicable only under conditions where adsorbable fluoride complexes are either not formed or show only negligible adsorption. Thus the computations probably apply

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(14) See *e.g.* (a) G. Jander and K. F. Jahr, *Kolloid-Beih.*, **41**, 27 (1935); (b) M. M. Jones, THIS JOURNAL, **76**, 4233 (1954).

(15) See *e.g.*, (a) L. G. Longsworth and D. A. McInnes, Report A-360, Nat. Defense Res. Committee, Office of Sci. Res. and Dev., Nov., 1942; (b) J. Sutton, J. National Res. Council of Canada No. 1612, Ontario, 1947; (c) K. A. Kraus and F. Nelson, Report AECD-1864, March, 1948; and (d) S. Ahrland, *Acta Chem. Scand.*, **3**, 371 (1949).

at high HCl concentrations where $D_F < D_{Cl}$, but they do not apply at low HCl concentrations where D_F may become equal to or even larger than D_{Cl}. In this region negatively charged fluoride complexes must be formed which are adsorbed by the resin. Using equation 6 the following values for $\Sigma(MF_i)_F/(m_t)_F$ were computed for 1*M* HF solutions

7 *M* HCl: W(VI) 0.92; Mo(VI) 0.72; U(VI) 0.52
11 *M* HCl: W(VI) 0.84; Mo(VI) 0.27; U(VI) <0.05

Thus the fraction of the metal complexed by fluoride ions at a given acidity is largest for W(VI), least for U(VI), with Mo(VI) lying intermediate, *i.e.*, this fraction does not follow the order of the elements in the periodic table. Adsorbabilities at low HCl concentrations where D_F rises rapidly with decreasing *M* HCl and where $D_F > D_{Cl}$ follow the same pattern, *i.e.*, W(VI) shows highest adsorption, U(VI) least adsorption, although the difference between W(VI) and Mo(VI) is less marked than at high HCl concentrations.

No computations of the stability constants of the fluoride complexes of these elements will be given at this time since their determination involves detailed knowledge of the change of species in chloride solutions as well as variations of the activity coefficients with ionic strength, particularly at high HCl concentrations.

Acknowledgment.—The authors are greatly indebted to Mrs. L. W. Magnusson, Jr., for valuable technical assistance.

OAK RIDGE, TENN.

[CONTRIBUTION FROM VARIAN ASSOCIATES]

The Electron Withdrawal Power of Substituent Groups

BY B. P. DAILEY[1] AND J. N. SHOOLERY

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A study of chemical shifts in the nuclear magnetic resonance spectra of ethyl and methyl derivatives of a number of organic substituent groups has been made. It was desired to find out how the electronegativity of an atom changes when it forms a part of different substituent groups and to attempt to derive a table of the electron withdrawal power of the substituent groups. A simple relationship between proton "chemical shifts" and the ionic character of the chemical bond to the proton has been established by the regularities existing in the experimental results of this study. It is shown that the electron withdrawal power of a substituent group is largely determined by the electronegativity of the first atom in the group.

Introduction

The use of electronegativities as a guide in studying electron withdrawal effects in chemistry has at least one serious drawback. The electronegativity of an atom is accurately defined for an atom forming a diatomic molecule but it is difficult to predict the changes in electronegativity which an atom will experience when it forms part of a polyatomic molecule.

The present study of chemical shifts in nuclear magnetic resonances was undertaken to attempt to discover how the electronegativity of an atom changes when it forms a part of different substituent groups and if possible to derive a table of the electron withdrawal power of the substituent groups.

The magnetic resonance absorption of a proton chemically bonded to another atom in molecule occurs at a value of the magnetic field which is influenced by the electronic structure of the molecule. The theoretical discussion of the calculation of chemical shifts presented by Saika and Slichter[2] makes it appear that the chemical shifts for protons can be rather simply related to the ionicity of the chemical bond to the proton. They divide the contributing factors into three terms: (1) the diamagnetic correction for the atom in question arising largely from the bonding electron during the period it occupies an atomic 1s orbital centered about the proton (2) the paramagnetic term for the atom in question. This term should be zero for an atomic 1s orbital. (3) The contribution from other atoms.

For a given chemical bond such as the C–H bond, the largest contribution of the type designated as (3) above should remain constant so that as different substituent groups are bonded to the carbon atom the shifts in the proton magnetic resonance can be used to measure the change in the ionicity of the C–H bond and the relative electron withdrawal power of the substituent groups.

The assumption of a simple relationship between shifts in proton resonances and the ionic character of the chemical bond to the proton is plausibly suggested by theoretical considerations but must, of course, be justified by regularities demonstrated in the experimental data. Such regularities were apparently established for ethyl derivatives in an earlier paper[3] and also by an analysis of the data of Meyer, Saika and Gutowsky.[4] However the results obtained in the more recent study by Meyer and Gutowsky[5] of methyl derivatives seemed to contradict the above generalizations. The object of this study was to measure the shifts in the proton magnetic resonances in the methyl and ethyl derivatives of a number of substituent groups so that the relations between the shifts and ionicity might be more firmly established and that these groups might therefore be arranged in order of their electron withdrawal power. Alternatively,

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