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Contract No. W-7405-eng-48

ANION EXCHANGE OF COMPLEX FLUO-IONS OF ZIRCONIUM AND HAFNIUM

E. H. Huffman and R. C. Lilly

August 23, 1950

Berkeley, California

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ABSTRACT

The elution of complex fluo-ions of zirconium and hafnium from an anion exchange resin with mixtures of hydrochloric and hydrofluoric acids has been studied in two different concentration ranges. Differences in the dependence of the distribution coefficient upon both the chloride ion concentration and upon the hydrofluoric acid concentration have been noted for the two ranges, and some possible ionic equilibria are discussed in connection with the data.

ANION EXCHANGE OF COMPLEX FLUO-IONS OF ZIRCONIUM AND HAFNIUM

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The separation of zirconium and hafnium by anion exchange of their negative fluo-ions has been reported by Kraus and Moore[1] and by Huffman and Lilly.[2]

(1) K. A. Kraus and G. E. Moore, J. Am. Chem. Soc., 71, 3263 (1949).

(2) E. H. Huffman and R. C. Lilly, J. Am. Chem. Soc., 71, 4147 (1949).

The former investigation made use of the resin Dowex-1 and an eluting solution composed of 1.0M hydrochloric acid and 0.5M hydrofluoric acid (referred to herein as high acid concentration); the latter investigation made use of the resin Amberlite IRA-400 and an eluting solution composed of 0.2M hydrochloric acid and 0.01M hydrofluoric acid (referred to herein as low acid concentration). Moore and Kraus have also presented data to show the dependence of the rate of elution upon the hydrochloric acid and the hydrofluoric acid concentrations in the high acid concentration range,[3] though it is not clear from this work whether

(3) G. E. Moore and K. E. Kraus, Division of Physical and Inorganic Chemistry, American Chemical Society, Detroit, Michigan, April 18, 1950.

the rate of elution is dependent upon both the hydrogen ion concentration and the chloride ion concentration or only upon the latter.

Work in this laboratory has shown that the dependence of the elution rate upon the acid concentrations is not the same for the two different mixed acid concentration ranges. This paper presents the results of this work and discusses possible ionic species involved in the exchanges. Data have been obtained in the low acid concentration range to show the elution rate dependence upon

chloride ion concentration, hydrogen ion concentration, and hydrofluoric acid concentration. Data have also been obtained in the region studied by Moore and Kraus,[3] but using lithium chloride as well as hydrochloric acid in order to obtain the effect due to chloride ion alone. The present data were obtained using macro quantities of zirconium and hafnium, and Amberlite IRA-400 in place of Dowex-1.

EXPERIMENTAL

Preparation of the Adsorbent.-- Amberlite IRA-400 resin, as received from the manufacturer, was in the chloride form. The air-dried material was ground and dry screened to obtain 200/325 mesh particles and washed free of fines by decantation with water in a beaker. Columns of 6.5 mm. i.d. were bored from 15 cm. lengths of lucite rod and threaded externally at both ends. The lower end was fitted with a lucite cap having a capillary tip and the upper end was fitted with a cap to which 6 mm. i.d. tygon tubing could be attached. Teflon gaskets were used to seal the fittings. A small cotton plug was inserted at the bottom of the column and the resin was washed in to give a bed length of 10.5 cm. after gentle tapping.

The free column volume was determined in the following manner. Upon completion of a run the resin was removed from the column, dried at 110° and weighed. The true volume of the resin particles was obtained by using this weight and the density given by the manufacturer. Subtracting this volume from the apparent volume of the column bed gave the free volume. In some instances the air-dried resin was weighed before it was put in the column. The results of six determinations using water, eluting solutions in the low concentration range and eluting solutions in the high concentration range gave a value of 2.3 ± 0.1 ml. for the free volume of the column described above.

Preparation of the Solutions.-- Johnson, Matthey and Co. zirconium metal was dissolved in hydrofluoric acid, the solution was evaporated and the residue was ignited to the oxide. Spectrographic analysis showed a 0.4% hafnium content based on the zirconium. Chemical Commerce hafnium nitrate, containing 0.3% zirconium, was dissolved in dilute hydrochloric acid, precipitated with ammonium hydroxide, washed with water and ignited to the oxide. Weighed quantities of hafnium and/or zirconium oxide were dissolved in a mixture of hydrofluoric and nitric acids in a platinum dish, tracer solution was added and the solution was fumed with sulfuric acid. This solution was then transferred to a Lusteroid tube with water and precipitated with ammonium hydroxide. The precipitate was centrifuged, washed with water and again centrifuged. The metal hydroxide was dissolved in enough hydrofluoric acid to give a final solution of approximately 0.06M hydrofluoric acid.

Zirconium tracer solutions were prepared from carrier-free Zr^{95} which was received in 10M nitric acid and 5% oxalic acid. This solution was diluted to about 8M nitric acid, a small amount of 0.5M potassium permanganate was added and the solution was heated in a water bath to precipitate manganese dioxide which carries the daughter Nb^{95}. The mixture was centrifuged and the supernatant liquor filtered. Tracer Hf^{181} solutions were prepared from pile-neutron irradiated hafnium dioxide in the same way as were the hafnium and zirconium solutions above. These tracers were obtained from the Isotopes Branch, United States Atomic Energy Commission.

In the experiments where only one element was needed to show the dependence of the distribution coefficient on various eluting solutions, hafnium was chosen in order to avoid periodic separation of the daughter Nb^{95} which would be necessary if Zr^{95} were used.

Adsorption and Elution.-- Column runs were made both with mixtures of zirconium and hafnium and with hafnium alone. Adsorptions were carried out from 5 ml. of 0.06M hydrofluoric acid onto 60 mg. of resin by shaking for one and one-half hours in a Lusteroid tube sealed with a paraffin coated cork. The tube and contents were centrifuged, the supernatant solution was poured off, and the resin was washed once with 5 ml. of water. Tracer counting of the supernatant solution and wash showed 98.0-99.8% adsorption. The amount of zirconium used was always 2.0 mg. with about 1.5×10^6 counts per minute of Zr^{95}. In order to get the same count of Hf^{181}, the amount of carrier hafnium varied from 1.0 mg. to 2.8 mg. The resin containing the adsorbed complex was slurried onto the prepared column of resin with water and the liquid level brought just to the top of the resin.

The eluting solutions were contained in discarded hydrofluoric acid bottles made of plastic and were run into the columns through Tygon tubing after carefully filling the column above the resin with the eluting solution. All runs were made at a flow rate of 2.8 ± 0.2 ml. per hour and the elutriant was collected in Lusteroid tubes at from 7.5 minute to 60 minute intervals by means of an automatic sampler. Aliquots of the tube contents were evaporated on platinum discs and counted in a G.M. counter in order to obtain the concentration of solute.

DISCUSSION

The effect of varying the hydrochloric acid concentration in the low acid range is shown in Fig. 1. The elution rate is not only greater with higher concentration, but the peaks are also sharpened and the valleys between are raised. Identification of the zirconium and hafnium peaks were made both by the total counts under them and by spectrographic analysis. As it was not obvious

that the results given by Kraus and Moore[1] in the high acid concentration range would be the same on Amberlite IRA-400 as on Dowex-1, their separation was repeated on a column as described above. The results of this separation are shown in Fig. 2. The solid part of this curve was obtained by counting Zr^{95} and Hf^{181} tracers and the dotted parts by a combination of spectrographic analysis and tracer analysis. The difference in appearance of the curves in the two acid concentration ranges suggests that the mechanisms may be different.

It has been shown by Mayer and Tompkins[4] for ion exchange processes that

(4) S. W. Mayer and E. R. Tompkins, J. Am. Chem. Soc., 69, 2866 (1947).

$$D = \frac{V_{max}}{v}, \qquad (1)$$

where D is the distribution coefficient between the resin and the solution in contact with it, V_{max} is the volume of elutriant that has been collected at the peak concentration (after subtracting one free column volume which does not pass through the adsorbed solute) and v is the free column volume. The reaction for eluting a complex fluo-ion of zirconium from an anion exchange resin with a solution of hydrochloric and hydrofluoric acids may be written as

$$R_nH_xZrF_y + mH^+ + nCl^- = H_pZrF_z^{4+p-z} + nRCl + (y-z)HF \qquad (2)$$

where R represents a unit charge on the resin. No information is available concerning the activity coefficients for complex fluo-ions of zirconium and hafnium either in solution or on resins. However, Kressman and Kitchener[5] have shown

(5) T. R. E. Kressman and J. A. Kitchener, J. Chem. Soc., 1949, 1201.

that for cation exchangers the equilibria obey the law of mass action if concentrations are used instead of activities. The equilibrium constant for

reaction (2) in terms of molar concentrations is then

$$K = \frac{(H_pZrF_z^{4+p-z})(RCl)^n(HF)^{y-z}}{(R_nH_xZrF_y)(H^+)^m(Cl^-)^n} \qquad (3)$$

and, since (RCl) may be considered constant,

$$D = \frac{(R_nH_xZrF_y)}{(H_pZrF_z^{4+p-z})} = K' \frac{(HF)^{y-z}}{(H^+)^m(Cl^-)^n} . \qquad (4)$$

The values of D may be read from elution curves such as those shown in Fig. 1 at the volume of maximum concentration, according to equation (1).

If log D is plotted against log (Cl^-), with (H^+) and (HF) constant, the slope of the curve will give the value of n in Equations (2) and (4). The value of y-z may be obtained in a similar manner when (HF) is the variable. However, (H^+) can not be varied while (Cl^-) is kept constant by using another acid without introducing another competing negative ion. For this reason the effect due to change in (H^+) was obtained by varying (HCl) in one plot and then using varying concentrations of lithium chloride with constant (HCl) in another plot and taking the difference between the two slopes.

The results obtained by Moore and Kraus[3] show that the elution rate is independent of the hydrofluoric acid concentration and that it varies with the second power of the hydrochloric acid concentration. This could be interpreted as meaning that the elution rate depends upon the first power of the concentration of hydrogen ion as well as upon the first power of the chloride ion, leading to the following two possible reactions:

$$RZrF_5 + H^+ + Cl^- = HZrF_5 + RCl \qquad (5)$$

$$RHZrF_6 + H^+ + Cl^- = H_2ZrF_6 + RCl \qquad (6)$$

The alternative explanation, given by Moore and Kraus, is that the rate depends upon the second power of the chloride ion concentration, thus suggesting the reactions:

$$R_2ZrF_6 + 2Cl^- = ZrF_6^= + 2RCl \qquad (7)$$

$$R_2HZrF_7 + 2Cl^- = HZrF_7^= + 2RCl \qquad (8)$$

The data presented in Fig. 3 show a negative slope of 2.0 for the plot of log D vs. log (Cl^-) when lithium chloride is used in varying concentration with a fixed concentration of 0.60M hydrochloric acid, as well as when hydrochloric acid alone is the source of chloride. The concentration of hydrofluoric acid was maintained at 0.50M for these results. Since the elution rate is independent of the hydrogen ion concentration, the reactions given in Equations (5) and (6) are seen to be eliminated as possibilities. The elution rate has been found to be independent of hydrofluoric acid concentrations from 0.25M to 4.00M at a constant concentration of 1.00M hydrochloric acid on Amberlite IRA-400. Since this confirms the results previously found for tracer quantities on Dowex-1[3] the present data are not given here.

The picture presented in the low acid concentration range is somewhat different. The dependence of D on hydrofluoric acid concentrations from 0.005M to 0.40M at a constant hydrochloric acid strength of 0.23M is shown in Fig. 4. The slope of 1.1 for this curve shows that there is one less fluorine atom in the complex in solution than in the complex on the resin. The slope of -1.5 for the dependence of D on the chloride ion concentration is more difficult to interpret. This slope is shown in curve A of Fig. 5 for an eluting solution of 0.20M hydrochloric acid and 0.05M to 0.20M lithium chloride. Curve B shows a slope of -2.5 when hydrochloric acid alone is used as eluting solution. The difference between these slopes gives a first power dependence on the hydrogen

ion concentration, showing that hydrogen ion is used only in combining with the fluoride ion released when the complex is eluted from the resin.

If the slope of the log D vs. log (Cl^-) plot were an even-1.0, then the two reactions

$$RZrF_5 + H^+ + Cl^- = ZrF_4 + HF + RCl \qquad (9)$$

$$RHZrF_6 + H^+ + Cl^- = HZrF_5 + HF + RCl \qquad (10)$$

would be possibilities. Similarly a slope of-2.0 would allow the reactions

$$R_2ZrF_6 + H^+ + 2Cl^- = ZrF_5^- + HF + 2RCl \qquad (11)$$

$$R_2HZrF_7 + H^+ + 2Cl^- = HZrF_6^- + HF + 2RCl. \qquad (12)$$

The slope of-1.5 probably indicates that one of the reactions (9) or (10) and one of the reactions (11) or (12) are both operating in this elution. The present data are insufficient to clear up this point.

One thing further can be pointed out. It is highly unlikely that reaction (7) in the low acid concentration and reaction (12) in the high acid concentration can both be true, as this would require R_2ZrF_6 when the fluoride ion concentration in the solution is about 10^{-4}M and R_2HZrF_7 when the fluoride ion concentration is about 10^{-5}M. It would also call for $ZrF_6^=$ in about 1.0M hydrochloric acid and $HZrF_6^-$ in about 0.2M hydrochloric acid.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to John Conway and Milton Moore for the spectrographic analyses made in connection with this work and to Dr. Theodore Vermeulen for his valuable suggestions.

This work was done under the auspices of the U. S. Atomic Energy Commission.

Fig. 1.-- Elution of fluozirconate and fluohafniate with 0.009M hydrofluoric acid in (A) 0.23M hydrochloric acid, (B) 0.20M hydrochloric acid and (C) 0.17M hydrochloric acid.

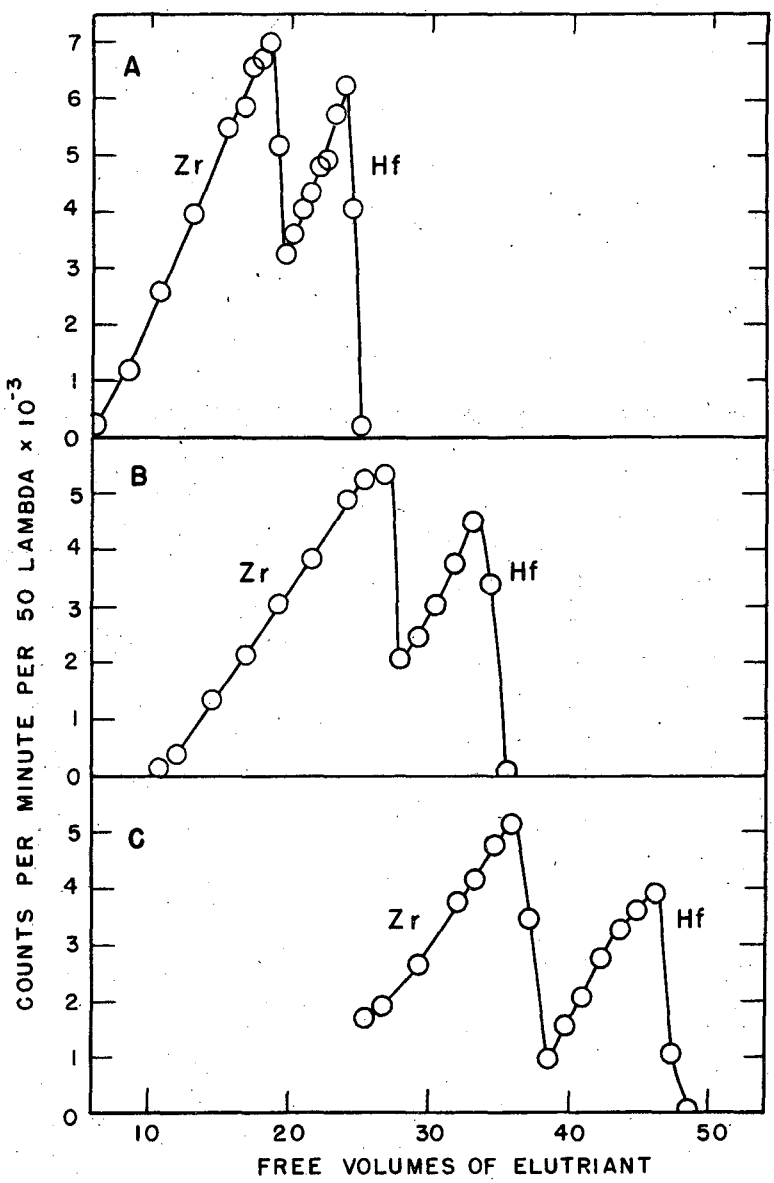

A
B
C
Zr
Hf
COUNTS PER MINUTE PER 50 LAMBDA x 10^-3
FREE VOLUMES OF ELUTRIANT
0
1
2
3
4
5
6
7
10
20
30
40
50

FIG. 1 MU 695

Fig. 2.-- Elution of fluozirconate and fluohafniate with 1.0M hydrochloric acid and 0.50M hydrofluoric acid; ○, tracer analysis; X, combined spectrographic and tracer analysis.

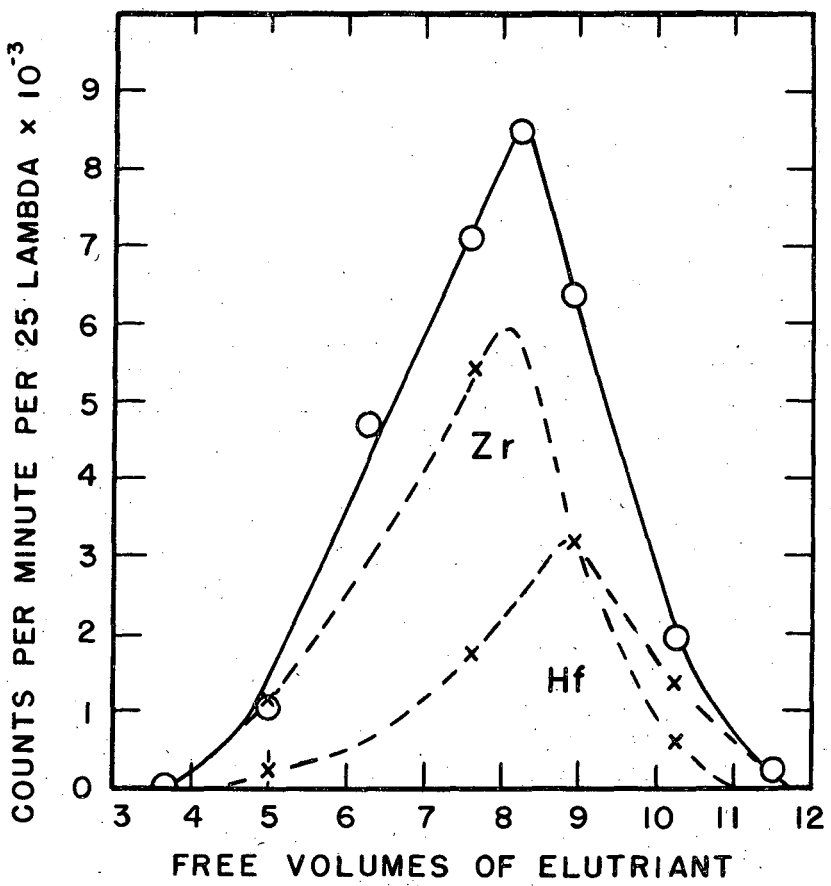
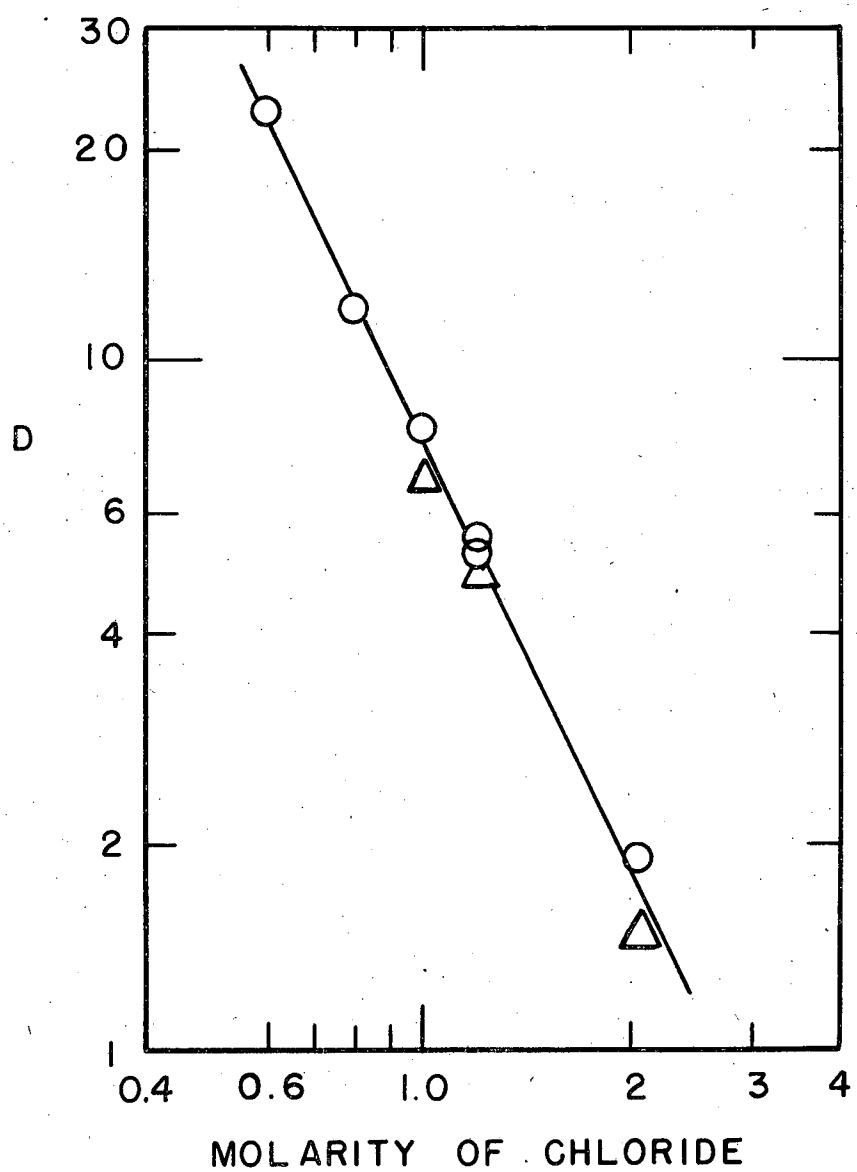

COUNTS PER MINUTE PER 25 LAMBDA x 10^-3
0
1
2
3
4
5
6
7
8
9
3
4
5
6
7
8
9
10
11
12
FREE VOLUMES OF ELUTRIANT
Zr
Hf

FIG. 2 MU 696

Fig. 3.-- Dependence of distribution coefficient of fluohafniate on chloride ion concentration; ○, hydrochloric acid with 0.50M hydrofluoric acid; Δ, lithium chloride with 0.60M hydrochloric acid and 0.50M hydrofluoric acid.



MU 697

FIG. 3

Fig. 4.-- Dependence of distribution ratio of fluohafniate on hydrofluoric acid concentration in 0.23M hydrochloric acid.

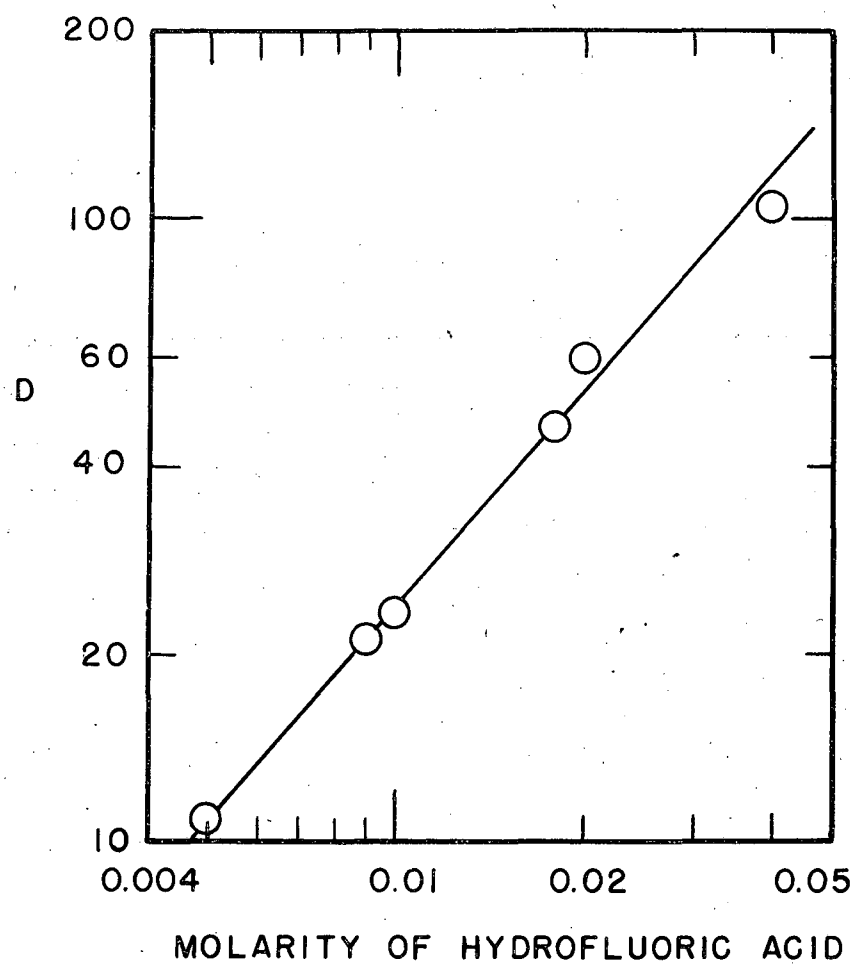

200
100
60
40
20
10
D
0.004
0.01
0.02
0.05
MOLARITY OF HYDROFLUORIC ACID

FIG. 4

MU 698

Fig. 5.-- Dependence of distribution coefficient on chloride ion concentration and on hydrochloric acid concentration; A, lithium chloride in 0.20M hydrochloric acid and 0.009M hydrofluoric acid (fluohafniate); B, hydrochloric acid and 0.009M hydrofluoric acid (fluohafniate); C, same as B for fluozirconate. Points for 0.17M, 0.20M and 0.23M hydrochloric acid taken from Fig. 1.

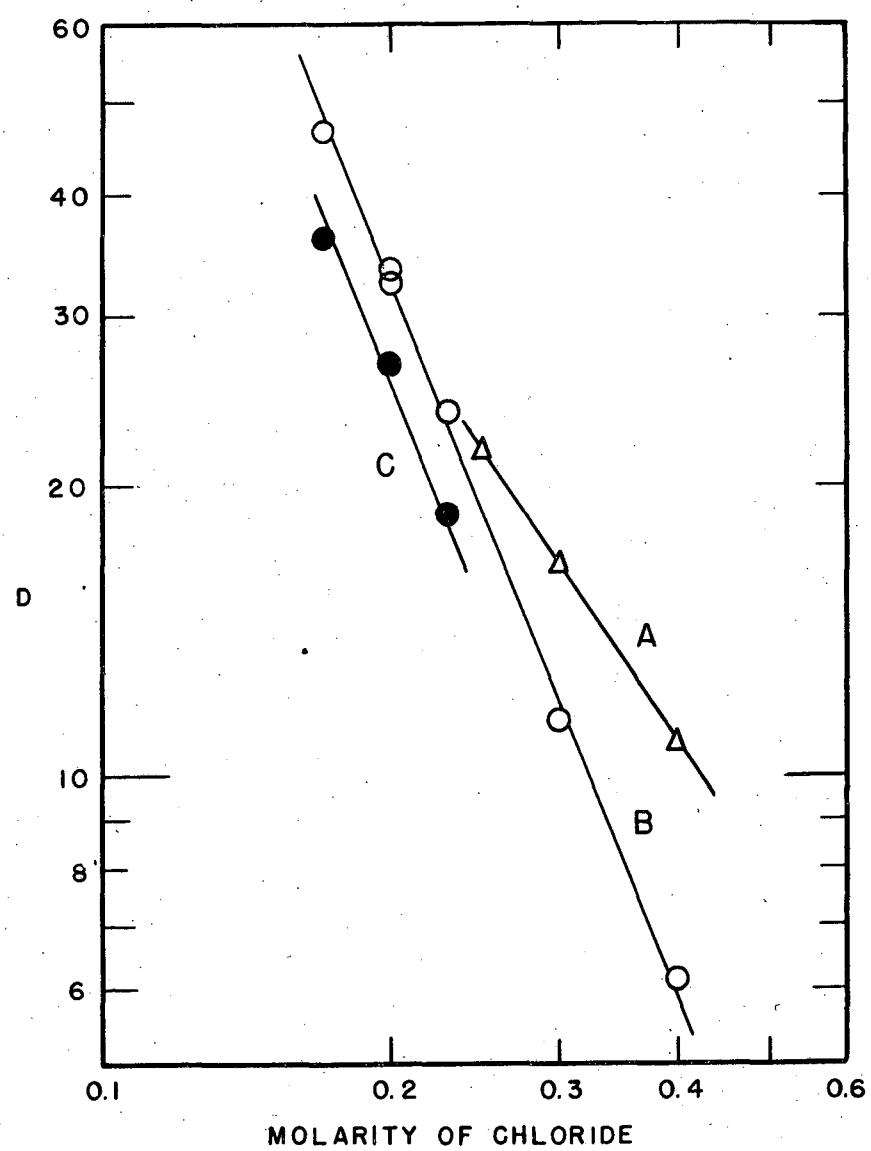


FIG. 5

MU 699