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INVESTIGATION OF THE TANTALUM FLUORIDE SYSTEM
USING THE FLUORIDE-SELECTIVE ELECTRODE

by

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ABSTRACT

Stability quotients for mono- through heptafluorotantalates in 2 M perchlorate at 25°C were calculated from measurements of free fluoride ion concentrations by the lanthanum fluoride membrane electrode. Ion exchange distribution measurements indicate that anionic fluoride complexes exist below $\bar{n} = 5$.

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INTRODUCTION

The nature and extent of fluoride complexing by tantalum in aqueous solution has been the subject of some investigation and discussion. Varga and coworkers[1,2,3] have reported the existence of the mononuclear ions TaF_4^+ through TaF_9^{4-} on the basis of potentiometric determination of H^+ , ion exchange, and solvent extraction studies. Results from these different techniques are not in complete agreement. A later similar potentiometric investigation by Bukhsh *et al.*[4] resulted in somewhat different stability quotients for the tantalum fluorides, with no evidence for the existence of TaF_9^{4-} .

The techniques of measurement in the previous works have precluded investigation of lower complexes of tantalum fluorides. However, recent development of an electrode that is selective for free fluoride (i.e., the lanthanum fluoride membrane ion-selective electrode[5]) has made feasible the investigation of the tantalum fluoride system in the region where lower fluoride species would occur. Experimental measurements with the electrode can be extended into the region covered by the other techniques.

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This paper describes an investigation of the tantalum fluoride system, particularly in the lower fluoride concentration region, at 25°C in 2 M perchlorate and at free acid concentrations greater than 0.15 M. Stability quotients were calculated for the tantalum fluoride complexes from potentiometric measurements with the fluoride-selective electrode. The cationic or anionic nature of the tantalum fluoride species in these experiments was inferred from ion exchange distribution experiments.

EXPERIMENTAL

Reagents

The chemicals were reagent-grade. Solutions were made up in deionized water, and their concentrations established by conventional analytical methods. Prolonged contact of fluoride solutions with glass was avoided, and all solutions were stored in polyethylene. Quinhydrone was prepared from quinone and hydroquinone and recrystallized from time to time.

K_2TaF_7 crystals (K & K Laboratories, Inc., Plainview, N. Y.) assayed 98.25 ± 0.95% in nine determinations by the method of Hague and Machlan[6]. Determination of total fluoride content by the method described below provided variable fluoride contents, 95 to 100% of the theoretical value. No correlation of assay results was found with mode of preparation of the salt: as received, dried at 120°C several hours, or recrystallized from HF followed by drying. The theoretical formula weight of 392 for K_2TaF_7 was used in the calculations.

The fluoride content of the solid K_2TaF_7 was determined by a method that was suggested by the observation that treatment of a Pa(V) compound with excess ammonium hydroxide quantitatively releases the anion, e.g., F^- [7]. Weighed

amounts of finely divided K_2TaF_7 were allowed to stand overnight in contact with excess concentrated ammonium hydroxide. The tantalum oxide solids were then removed by filtration, an equal volume of ethanol was added to the filtrate, and the solution was neutralized with HNO_3 to the first color change of methyl red indicator. The alcoholic solutions were then titrated potentiometrically with standard $La(NO_3)_3$ solution, with the fluoride-selective electrode as indicator electrode. Results within a set of determinations were generally precise, but, as noted above, they were not always consistent from one set to another.

Formation Curve

Potential measurements were made with an Orion Model 801 Digital pH/mV Meter.* Fluoride ion was determined with the Orion Fluoride Ion Activity Electrode, No. 94-09, and the Double Junction Reference Electrode, No. 90-02, the outer chamber of which was filled with 2 M NaCl. The hydrogen ion was determined with this same reference electrode and a gold** -quinhydrone electrode. Glass electrodes gave unstable readings in the acidic fluoride solutions and could not be used. The quinhydrone in solution did not affect the potential of the fluoride-reference electrode pair.

The fluoride electrode was calibrated daily in standard 4×10^{-4} M NaF in 2 M $NaClO_4$. The Nernstian response of the electrode has been established[5]. The quinhydrone electrode was not calibrated, because only differences in acidity were required; a Nernstian response was assumed.

* Orion Research Incorporated, Cambridge, Mass.

** Beckman No. 39276, Beckman Instruments, Inc., Fullerton, California.

Calibration of the fluoride electrode in neutral solution, followed by measurements in acidic experimental solutions, caused an appreciable change in the liquid junction potential of the reference electrode. Evaluation of this change was determined in separate measurements with a solid-state iodide-selective electrode and iodide in solution[8]. The change in liquid junction potential, ΔE_j , as a function of acid concentration is given in Figure 1.

The experimental solutions were stirred in polypropylene beakers that were partially immersed in a water bath at 25°C. For each set of experimental points, a preliminary determination was made of the potentials of the fluoride-reference and quinhydrone-reference electrodes in 20 to 50 ml of a determinate mixture of HF (or NaF), HClO_4 , and NaClO_4 with a total ionic strength of 2 M. Then, a weighed amount of powdered K_2TaF_7 was added. (Early experiments in which solutions of K_2TaF_7 in HClO_4 or NaClO_4 were added gave erratic results.) The potentials of the fluoride-reference and quinhydrone-reference electrodes were monitored until they reached steady values (about 30 minutes) and until no undissolved crystals remained. Each solution was examined under a strong light for evidence of cloudiness; data from the infrequent cloudy solution was discarded.

Use of K_2TaF_7 as the source of tantalum imposed a lower limit on the free fluoride concentrations that could be attained. To obtain lower concentrations, zirconium, as 0.1062 M $\text{ZrO}(\text{ClO}_4)_2$ in 1 M HClO_4 , was added to the tantalum solution as a fluoride scavenger. Potential response was immediate and steady, and no cloudiness occurred.

Ion Exchange

For the ion exchange studies, "Amberlite"* IR-120 and "Amberlite"* IRA-400 were first converted to the sodium and perchlorate forms, respectively, and then preconditioned by equilibration with solutions that simulated the test solutions but did not contain tantalum. The composition of the final resin pretreatment mixture was adjusted with 0.1 M NaF in 2 M NaClO₄ to give the same potential reading with the fluoride electrode as the test solution with which the resin was to be equilibrated.

The pre-conditioned resin was then dried with filter paper, and about 4 grams were added to about 25 ml of the test solution, which contained tantalum. After more than 2 hours stirring at 25°, the solution was decanted from the resin. Aliquots of the test solution, before and after the resin treatment, were made ammoniacal and left overnight, and the total fluoride content was determined as described above.

INTERPRETATION OF DATA

The fluoride electrode was calibrated in 2 M NaClO₄ that contained known amounts of NaF, and the free fluoride ion concentration in the test solution was determined by

$$F = F_{\text{std}} \exp\left(\frac{F}{RT}\right) (E_{\text{std}} - E_F - \Delta E_j) \quad (1)$$

where ΔE_j is the change in liquid junction potential of the reference electrode due to differing acidities in the standard and test solutions. E_{std} and E_F are the respective measured potentials.

* Trademark of Rohm and Haas Co.

Potential measurements were made before (Solution 1) and after (Solution 2) dissolution of a weighed amount of K_2TaF_7 in the determinate mixture of HF, $HClO_4$, and $NaClO_4$. At the low fluoride concentrations and high acidities, the only significant complex of fluoride with hydrogen is HF. Hence, potential measurements for Solution 1 and Solution 2 can be combined to give

$$\begin{aligned} (HF)_2 &= (HF)_1 (F_2/F_1) (H_2/H_1) \\ &= (F_{T1} - F_1) \exp (g/RT) (E_{F1} - E_{F2} + E_{H2} - E_{H1}) \end{aligned} \quad (2)$$

The average number of fluoride ligands bound per tantalum atom, \bar{n} , was calculated by

$$\bar{n} = \frac{F_{T2} - F_2 - (HF)_2}{Ta_T} \quad (3)$$

The symbols represent concentrations of the respective species; the subscripts designate which test solution; and the subscript T indicates the total amount of that ion initially added to the system.

The experimental data were interpreted by the Bjerrum formulation[9], assuming successive formation of mononuclear complexes, whence

$$\bar{n} = \frac{\sum_{i=1}^n i \beta_i F^i}{1 + \sum_{i=1}^n \beta_i F^i} \quad (4)$$

and β_i , the over-all stability quotients, are related to the step stability quotients by

$$\beta_i = \prod_{j=1}^i k_j \quad (5)$$

and (e.g., for tantalum)

$$k_i = \frac{TaF_i^{5-i}}{(TaF_{i-1})^{6-i} (F)} \quad (6)$$

The term stability quotient is used in preference to stability constant because these equilibrium values involve concentrations, not activities.

When a solution of zirconium was added to the system to scavenge fluoride,

$$\bar{n}_{\text{Ta}} = \frac{F_{\text{T}_2} - F_2 - (\text{HF})_2 - \bar{n}_{\text{Zr}} \text{Zr}_{\text{T}}}{\text{Ta}_{\text{T}}} \quad (7)$$

The value of \bar{n}_{Zr} was calculated by Equation (4) with previously published stability quotients [10] for the zirconium fluorides in 2 M HClO_4 . The over-all stability quotients are given in Table I, where the published values have been combined with $k_{\text{HF}} = 1.3 \times 10^3 \text{ M}^{-1}$, the average value derived from the present work.

Over-all stability quotients for the tantalum system were calculated by numerically fitting the \bar{n} and free fluoride ion concentrations of Table II to Equation (4) by the computer program used in previous work (11), which minimizes the partial differential of \bar{n} with respect to each β_i .

RESULTS AND DISCUSSION

Formation Curve and Stability Quotients

Experimental results of Table II are shown in Figure 2 as a Bjerrum formation curve, where \bar{n}_{Ta} , the average number of fluoride ligands per tantalum atom, is plotted as a function of the free fluoride ion concentration. Use of the Bjerrum interpretation assumes that mononuclear species are formed by sequential addition of fluoride ligands. This assumption is more or less justified by the lack of marked dependence of the experimental results on tantalum concentration over the limited range of tantalum concentration covered.

The presence or absence of hydrolytic species has not been established with certainty. As seen in Figure 2, there is some effect of acid concentration at $\bar{n} \approx 4$, where data points at high acid are significantly displaced to lower fluoride concentrations. In this region, the large subtractive correction for HF, which increases with both fluoride concentration and acidity, may cause a substantial error. Otherwise no trend with acidity is apparent. The tantalum concentrations are so low, compared to the acid concentrations, that hydrolysis would not cause a detectable change in acidity. The data points obtained at 0.5 M H^+ (the triangles in Figure 1) were not included in the fit of the data.

Over-all stability quotients for the tantalum fluorides from $i=1$ to 7 are given in Table III. These were obtained from the numerical fitting of the formation curve; the fitted curve is drawn in Figure 1.

The first column in Table III shows the β values obtained when all $\beta_i > 0$. The ratio of β_6/β_5 (i.e., k_6) is much less than its neighboring ratios. As suggested by Rossotti[12], the data were recalculated, assuming $\beta_6 = 0$, to see if equally satisfactory agreement would be obtained. The second column in Table III shows that the other β values are essentially unchanged when $\beta_6 = 0$. Actually the fit is slightly improved.

The phenomenon of low or nonexistent values of β_6 is similar to that encountered by Varga[3] when he made a computer fit of the combined data from his potentiometric, anion exchange, and solvent extraction data. These β values are also included in Table III where they have been normalized to β_4 for comparison.

Thus, in dilute aqueous solutions of tantalum, existence of the hexafluorotantalate ion is not certain. One might conjecture the transformation

from TaOF_5^{2-} (ion exchange evidence below suggests an ion such as this) to TaF_7^{2-} , with no significant formation of TaF_6^- intermediate. Physical methods, such as ^{19}F nuclear magnetic resonance and Raman spectroscopy by which others [13,14] have observed TaF_6^- in solutions more concentrated in tantalum and fluoride, are not sufficiently sensitive to detect and identify ionic species in our system.

Our values of step stability quotients are compared with published values in Table IV. Varga and coworkers have given values from the potentiometric hydrogen ion determinations and the anion exchange distribution of ^{182}Ta tracer. Bukhsh *et al.* [4] repeated Varga's potentiometric experiments.

Poor agreement of the other step stability quotients at the lowest i values with their counterparts in this work would be expected. The other workers obtained β_i values and had to assume $\beta_i = k_i$ for the lowest complex. In any region except $\bar{n} < 1$, it is doubtful that one complex is sufficiently predominant to justify this assumption. The present work provides experimental data into the region of the monofluoro complex to provide a more satisfactory base point from which to derive step stability quotients of the lower fluoride complexes.

Agreement in the region of $\bar{n} = 5$ to 7 is encouraging, however. When β_6 is zero, only the ratio β_7/β_5 is meaningful; this is numerically the same as $k_6 k_7$ when $\beta_6 \neq 0$. The ratio of β_7/β_5 for the three sets of potentiometric data are all the same order of magnitude. The solvent extraction data [2] do not agree. The nature of the fundamental tantalum species may vary with experimental conditions.

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Ion Exchange Distribution

Qualitative indication of the anionic or cationic nature of the tantalum fluoride complexes in the experimental solutions was sought by determining the decrease in total fluoride concentration on batch equilibration with ion exchange resins. The composition of the solutions was typical of those used to establish the formation curve, i.e., 2 M ionic strength in NaClO_4 . The free fluoride ion concentration was established by potentiometric measurement, and the corresponding \bar{n} was read from the formation curve. The amount of tantalum-bound fluoride was thus $\bar{n}\text{Ta}_T$.

The change in total fluoride content of the solution was attributed to the absorption of the tantalum-fluoride complexes by the resin. The potential of the fluoride-reference electrodes changed less than 2 mV when the resin and solution were mixed, which provided reasonable assurance that ion exchange of simple fluoride ion was small.

In Table V, the small fraction of fluoride absorbed by the cation exchange resin indicates that anionic tantalum fluoride species predominate in the systems investigated. Simple fluoride complexes would all be cationic below $i=5$. The apparent anionic nature for $\bar{n} = 2.7$ suggests the fluoride complexes contain hydrolyzed tantalum species.

The presence of hydrolyzed tantalum would not be surprising for this small highly charged cation in solutions of limited concentration and acidity. Tantalum oxyfluorides are known in solid compounds, and have been observed in solutions containing <0.1 M HF [14]. On the other hand, Varga and Freund [1] assumed no hydrolysis, with TaF_5 the neutral species, for interpretation of their anion exchange experiments in 1 M HClO_4 .

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TABLE I

OVER-ALL STABILITY QUOTIENTS OF ZIRCONIUM FLUORIDES
IN 2 M HClO_4 *

β_1	8.20×10^8
β_2	2.23×10^{16}
β_3	1.91×10^{22}
β_4	1.76×10^{27}

* Recalculated from Ref. [9] with $k_{\text{HF}} = 1.3 \times 10^3 \text{ M}^{-1}$

TABLE II
TANTALUM-FLUORIDE EQUILIBRIUM DATA
in 2 M (HClO₄ + NaClO₄) at 25°C

F _T	H _T	Concentration, mM			F	\bar{n}
		Ta _T	Zr _T	HF		
8.172	242.1	1.117	3.65	0.0761	0.000270	0.434
4.787	160.6	0.631	1.54	0.2477	0.001194	0.915
3.069	221.1	0.387	0.94	0.3000	0.001049	1.063
4.804	157.5	0.633	1.16	0.5885	0.002899	1.298
7.365	164.8	0.878	1.92	0.6110	0.003122	1.542
4.821	154.5	0.635	0.78	1.289	0.006465	1.588
8.434	214.2	1.153	1.86	0.9280	0.003375	1.613
10.02	223.9	1.381	1.86	2.831	0.006194	1.656
4.840	151.3	0.638	0.39	2.393	0.01239	1.691
6.029	221.2	0.810	0.94	1.640	0.005489	1.744
3.069	221.1	0.387		2.344	0.008940	1.851
6.083	214.2	0.817		4.622	0.01633	1.877
20.17	344.4	2.689		15.07	0.02944	1.887
10.02	223.9	1.381	1.31	2.831	0.01039	1.970
10.06	221.2	1.386	0.94	3.839	0.01764	2.055
4.588	148.2	0.640		3.498	0.01835	2.095
19.40	577.1	1.752		15.58	0.02103	2.172*
15.42	285.9	1.701		11.65	0.02692	2.201
8.434	214.2	1.153		5.867	0.02247	2.207
7.705	157.1	0.886	0.97	2.349	0.01253	2.220
7.417	214.2	1.008		5.056	0.01930	2.324
18.71	287.0	1.678		14.72	0.03321	2.359
22.79	215.7	2.996		14.92	0.05108	2.612
7.776	149.3	0.894		5.300	0.02951	2.736
41.77	577.1	4.948		27.88	0.03830	2.800*
44.02	215.7	6.028		27.05	0.09303	2.800
18.72	214.2	2.624		11.13	0.04493	2.881
44.25	219.8	5.039		29.14	0.1057	2.976
36.44	289.0	3.248		26.46	0.05729	3.055
64.81	224.8	6.738		42.98	0.1655	3.270
53.41	224.8	5.110		35.87	0.1378	3.406
62.34	224.8	6.386		40.01	0.1519	3.474
70.80	229.7	6.399		46.32	0.1714	3.799
85.47	234.4	7.338		56.72	0.2115	3.889
54.89	572.1	2.724		44.08	0.06063	3.945*
79.00	572.1	6.168		54.32	0.07569	3.989*
88.35	238.9	6.623		60.67	0.2304	4.139
99.83	572.1	4.027		82.29	0.09340	4.333*
89.18	241.2	6.205		61.79	0.2322	4.376
92.41	243.3	6.131		64.32	0.2661	4.539
101.0	290.1	5.995		73.30	0.2501	4.576
118.4	305.9	3.863		98.83	0.3335	4.970
79.07	290.1	2.865		64.47	0.2756	5.000
147.8	305.9	8.072		105.5	0.3576	5.200
172.4	319.7	7.577		129.3	0.5118	5.621
183.3	325.8	7.340		140.9	0.5405	5.719
197.7	331.6	7.685		148.7	0.6051	6.291
205.3	285.0	6.505		162.9	0.9805	6.364
194.4	337.1	5.635		157.8	0.6267	6.387
184.0	285.0	3.444		160.7	0.9542	6.475
265.4	365.0	3.667		239.8	1.397	6.601
518.3	621.9	6.386		472.9	2.153	6.710
545.8	621.9	10.320		471.5	2.144	7.000

* High free acid concentration; not included in fit

TABLE III

OVER-ALL STABILITY QUOTIENTS OF THE TANTALUM FLUORIDE SYSTEM AT 25°C

	This Work		Ref. [2]*	Ref. [3]* (Combined data of Ref. [1] and [2])
	$\beta_6 > 0$	$\beta_6 = 0$		
β_1	2.33×10^6	2.34×10^6		
β_2	7.08×10^{11}	7.07×10^{11}		
β_3	1.06×10^{16}	1.07×10^{16}		
β_4	4.31×10^{19}	4.27×10^{19}	$4.3 \times 10^{19*}$	$4.3 \times 10^{19*}$
β_5	1.93×10^{23}	1.94×10^{23}	$3.5 \times 10^{24*}$	$3.7 \times 10^{24*}$
β_6	8.32×10^{24}	0	$2.8 \times 10^{29*}$	0
β_7	1.61×10^{30}	1.62×10^{30}	$8.2 \times 10^{33*}$	$4.6 \times 10^{32*}$
β_8	-	-	-	0
β_9	-	-	-	$9.3 \times 10^{38*}$

* Normalized to β_4 of This Work

TABLE IV

STEP STABILITY QUOTIENTS OF THE TANTALUM FLUORIDE SYSTEM AT 25°C

Source	Ref. [1]	Ref. [2]	Ref. [4]	This Work
Method	Potentiometric (H ⁺) and Ion Exchange	Solvent Extraction	Potentiometric (H ⁺)	Potentiometric (F ⁻)
Medium	1 M Perchlorate	3 M HClO ₄	1 M Perchlorate	2 M Perchlorate
Stability Quotients				
k ₁				2.3 x 10 ⁶
k ₂				3.0 x 10 ⁵
k ₃				1.5 x 10 ⁴
k ₄		7.3 x 10 ⁵		4.0 x 10 ³
k ₅	6.47 x 10 ⁴	8.1 x 10 ⁴		4.5 x 10 ³
k ₆	4.13 x 10 ³	8 x 10 ⁴	5.6 x 10 ³	0
k ₇	2.20 x 10 ³	3 x 10 ⁴	1.27 x 10 ³	
k ₈	9.39 x 10 ²		4.6	
k ₉	3.73 x 10 ³		-	
k ₆ k ₇ or β ₇ /β ₅ (see text)	9 x 10 ⁶	2.4 x 10 ⁸	7.1 x 10 ⁶	8.3 x 10 ⁶

TABLE V
ION EXCHANGE STUDY OF TANTALUM FLUORIDE SYSTEM

	Concentrations, M				\bar{n}_{Ta}	$F_T^{R^*}/F_T^O$	$\frac{\bar{n}_{Ta}/F_T^{O\dagger}}{1-F_T^R/F_T^O}$
	F_T^O	H_T	Ta_T	F^-			
Cation Exchange	0.0097	0.214	0.00139	3.1×10^{-5}	2.35	1.02	0
	0.0222	0.214	0.00317	6.13×10^{-5}	2.72	0.983	0.044
	0.137	0.276	0.00473	5.4×10^{-4}	6.0	0.994	0.029
Anion Exchange	0.0255	0.214	0.00364	5.95×10^{-5}	2.7	0.945	0.142
	0.138	0.305	0.00517	4.68×10^{-4}	5.7	0.940	0.281

* F_T^R = total fluoride in solution after resin equilibration

† Fraction of tantalum-bound fluoride absorbed by resin

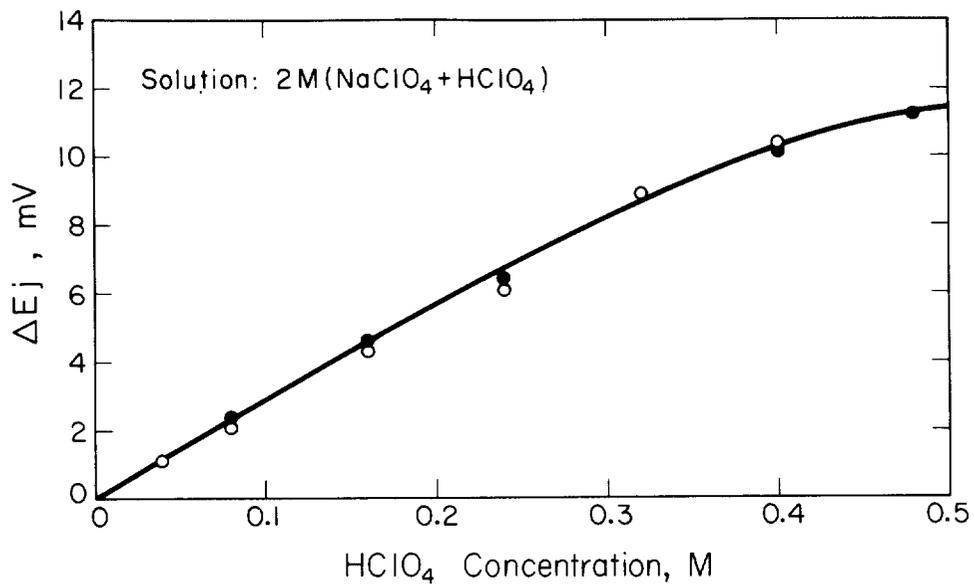


FIG. 1 CHANGE IN LIQUID JUNCTION POTENTIAL WITH HClO₄ CONCENTRATION

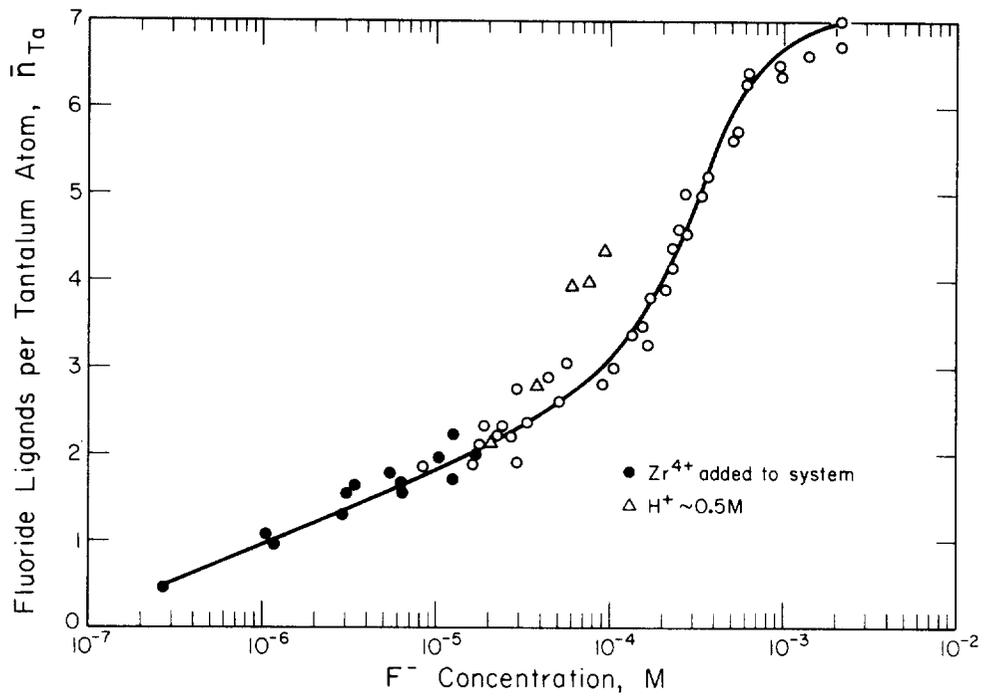


FIG. 2 TANTALUM FLUORIDE SYSTEM IN 2 M PERCHLORATE