

Anion Exchange Behaviour of Zr, Hf, Nb, Ta and Pa as Homologues of Rf and Db in Fluoride Medium

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Abstract. Studies of the chemical property of transactinide elements are very difficult due to their short half-lives and extremely small production yields. However it is still possible to obtain considerable information about their chemical properties, such as the most stable oxidation states in aqueous solution, complexing ability, etc., comparing their behaviour with their lighter homologous in the periodic table. In order to obtain a better knowledge of the behavior of rutherfordium, Rf (element 104), dubnium, Db (element 105) in HF medium, the sorption properties of Zr, Hf, Nb, Ta and Pa, homologues of Rf and Db, were studied in $\text{NH}_4\text{F}/\text{HClO}_4$ medium in this work. Stability constants of the fluoride complexes of these elements were experimentally obtained from K_d obtained at different F^- and H^+ concentrations. The anionic complexes: $[\text{Zr}(\text{Hf})\text{F}_5]^-$, $[\text{Zr}(\text{Hf})\text{F}_6]^{2-}$, $[\text{Zr}(\text{Hf})\text{F}_7]^{3-}$, $[\text{Ta}(\text{Pa})\text{F}_6]^-$, $[\text{Ta}(\text{Pa})\text{F}_7]^{2-}$, $[\text{Ta}(\text{Pa})\text{F}_8]^{3-}$, $[\text{NbOF}_4]^-$ and $[\text{NbOF}_5]^{2-}$ are present as predominant species in the HF range over investigation.

Key words: Rutherfordium, Dubnium, HF, Anion exchange, Zr, Ta, Nb.

Resumen. El estudio de las propiedades químicas de los elementos transactínidos conlleva grandes dificultades a nivel experimental, debido a las cortas vidas medias de dichos elementos y a sus bajos rendimientos de producción. Sin embargo, es posible, obtener considerable información sobre sus propiedades químicas, tales como su estado de oxidación más estable en solución acuosa, su habilidad de complejación, etc., comparando sus propiedades con las de sus homólogos más ligeros en la tabla periódica. A fin de tener un mejor conocimiento del comportamiento del rutherfordio Rf (elemento 104) y el dubnio Db (elemento 105) en medio HF, en este trabajo se estudiaron las propiedades de adsorción de los homólogos del Rf y Db: Zr, Hf, Nb, Ta y Pa en el medio $\text{NH}_4\text{F}/\text{HClO}_4$. Las constantes de estabilidad de los complejos a base de fluoruros de estos elementos fueron determinados experimentalmente a partir de valores de K_d , obtenidos a diferentes concentraciones de F^- y H^+ . Se estableció la presencia de los siguientes complejos aniónicos: $[\text{Zr}(\text{Hf})\text{F}_5]^-$, $[\text{Zr}(\text{Hf})\text{F}_6]^{2-}$, $[\text{Zr}(\text{Hf})\text{F}_7]^{3-}$, $[\text{Ta}(\text{Pa})\text{F}_6]^-$, $[\text{Ta}(\text{Pa})\text{F}_7]^{2-}$, $[\text{Ta}(\text{Pa})\text{F}_8]^{3-}$, $[\text{NbOF}_4]^-$ y $[\text{NbOF}_5]^{2-}$, a las concentraciones de HF consideradas en este trabajo.

Palabras clave: Rutherfordio, dubnio, HF, intercambio aniónico, Zr, Ta, Nb

Introduction

The very short lives and low production rates of the heaviest elements: rutherfordium, Rf (element 104), dubnium, Db (element 105) and seaborgium, Sg (element 106), make chemical studies difficult. However, it is possible to obtain considerable information about their chemical properties, such as the most stable oxidation states in aqueous solution, complexing ability, etc., comparing their behaviour with their lighter homologs in the periodic table. Rutherfordium and dubnium do start new transition series with properties similar to their Group (IV) (Zr and Hf) and V (Nb, Ta) and Pa, the latter being a pseudo-homolog of dubnium in the periodic table [1, 2, 3].

For very heavy elements which are not available in micro- or nanogram quantities, partition methods are practical way for determining complexing constants, which are based on reactions between two phases under static or dynamic conditions. Exchange methods offer the advantages of simplicity and rapidity, and are amenable to a broad selection of phase compositions and arrangements [4]. The specificity of anion exchange resins for negatively charged ions allows studying the behaviour of metals complexes charged negatively and the metal separation [5]. Vargas [6] and Noren [7, 8] have investigated the behaviour of the fluoride complexes of Ta^{5+} and Hf^{4+}

- Zr^{4+} , respectively, in HF media under 4 M perchloric acid solutions by potentiometric and solvent extraction methods. They showed that the species $\text{Hf}(\text{Zr})\text{F}_n$ with $n = 6$ [7, 8] and $[\text{TaF}_6]^-$ to $[\text{TaF}_6]^{4+}$ [6] are formed and exist simultaneously at equilibrium. Nevertheless, to simulate the experimental conditions applied in the studies of the chemical properties of rutherfordium and dubnium [9-11], the present work shows the absorption study of M^{4+} (Zr, Hf) and M^{5+} (Nb, Ta and Pa) ions into strong basic anion exchange resin, in mixtures of ammonium fluoride (NH_4F 10^{-3} to 10^{-2} M) and perchloric acid (HClO_4 3×10^{-3} – 2.5×10^{-2} M). These results allows obtaining better information of how these elements behave in HF medium and determining the stability constants of the fluoride complexes of these elements under the experimental conditions previously described.

Results and discussion

In previous paper, we have reported the behaviour of Zr, Hf, Ta, Nb and Pa in HF medium on anion exchanger [12]. These elements present relatively high distribution coefficients (K_d) in HF medium ($>10^5$ cm^3/g). The K_d values decrease rapidly for high HF concentrations and present a discontinuities near

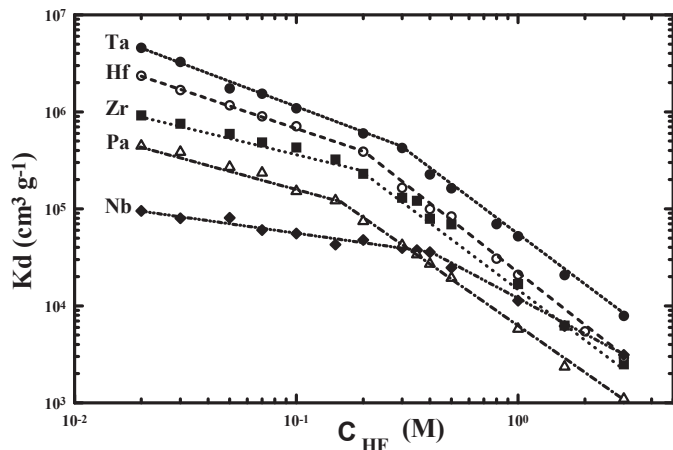


Fig. 1. Logarithmic variations of the K_d values as a function of logarithmic HF concentration for Zr, Hf, Nb, Ta and Pa. K_d values given in g/cm^3 . [12]

0.15 M (Zr and Pa) and 0.4 M (Ta and Nb) (See Fig. 1) which could not be explained quantitatively but appeared to be caused by evolution of the repartition of the complex populations which is function of F^- concentration and pH, independently [12]. This paper deals the sorption behaviour of these elements in pure HF from the point of view: i) of the slope break that the curves $\log K_d = f(\log[\text{HF}])$ and ii) of the possible species complexes formed in this medium. It was suggested the presence of the species $[\text{Zr}(\text{Hf})\text{F}_5]^-$ to $[\text{Zr}(\text{Hf})\text{F}_8]^{4-}$, $[\text{Pa}(\text{Ta})\text{F}_6]^-$ to $[\text{Pa}(\text{Ta})\text{F}_9]^{4-}$ and for niobium $[\text{NbOF}_4]^-$ to $[\text{NbOF}_7]^{4-}$ in hydrofluoric acid solutions [1, 6-8,13-17], and in the range over investigations the most probable species would be: $[\text{Zr}(\text{Hf})\text{F}_6]^{2-}$, $[\text{Pa}(\text{Ta})\text{F}_6]^-$ $[\text{Pa}(\text{Ta})\text{F}_7]^{2-}$ and for niobium $[\text{NbOF}_5]^{2-}$ [1, 6, 15-17]. However a satisfactory knowledge of the fluoride complexes of these elements in pure hydrofluoric acid medium is complicated by the fact that: i) HF is a weak acid, H^+ and F^- ion concentration vary simultaneously and the equilibria established between the species H^+ , F^- , HF_{free} and $[\text{HF}_2]^-$ in solution must be considered and ii) these complexes have a high dependence on $[\text{H}^+]$ and $[\text{F}^-]$ concentrations and special conditions are required to characterize these species. For this purpose, $\text{NH}_4\text{F}/\text{HClO}_4$ systems were chosen in order to establish the slope break of $\log K_d$ vs. $\log [\text{HF}]$, which could be interpreted in terms of the repartition evolution of the complex populations as function of F^- concentration and pH. NH_4F had been chosen so that it does not take part in the formation of any other species in the solution and establishes a definite ionic strength.

Curves $\log K_d = f(\log[\text{F}^-])$

The adsorbability for each element in the $\text{NH}_4\text{F}/\text{HClO}_4$ medium was measured in the solutions containing both reagents with different concentration combinations, varying from 3×10^{-3} to 5×10^{-2} M for NH_4F and 6.3×10^{-3} to 2.5×10^{-2} M for HClO_4 (see section 4). On base of these results, the variations of \log

$K_d = f(\log[\text{F}^-])$ for various pH's values were constructed and typical variation of these functions for Zr, Hf, Nb, Ta and Nb are shown in Fig. 2. The number of the each curve denotes the respective value of pH. The curves for Zr and Hf are very similar, whereas protactinium seems to resemble tantalum more than niobium.

As can be seen from comparison of the results in Fig. 2 the adsorption of all elements on AGMP1 in $\text{NH}_4\text{F}/\text{HClO}_4$ solutions is strongly influenced by the presence of $[\text{H}^+]$. The addition of $[\text{H}^+]$ to the solutions causes a strong decrease of the adsorbability. The curves of all elements have a concave form at all studied H^+ and F^- concentrations.

If M^{n+} (Zr^{4+} , Hf^{4+} , Nb^{5+} , Ta^{5+} and Pa^{5+}) species are assumed to be $[\text{M}(\text{Zr,Hf})\text{F}_6]^{2-}$ or $[\text{M}(\text{Ta,Nb,Pa})\text{F}_7]^{2-}$ in the aqueous solution, and if these species could be measured separately, then the plots of $\log K_d$ vs $\log[\text{F}^-]$ for each species should show straight lines with slope of -1,-2, -3, etc. respectively. However, the experimental variation of $\log K_d$ vs. $\log[\text{F}^-]$ does not present a straight line form (See Fig. 2). It could imply the simultaneous existence of more than two differently charged species in the solution.

In spite of the above discussion, it is difficult to specify the ionic charge of each species solely by analyzing the curves of $\log K_d$ vs. $\log[\text{F}^-]$. These phenomena could be connected with the formation or the presence of the dominating species which are less adsorbed on the resin (lower K_d values).

The stability constants k_j were evaluated from the functions $\log K_d$ vs. $\log[\text{F}^-]$, following the method described in section 4. The experimental procedure includes the determination of the values of K_d at different $[\text{F}^-]$ at pH constant. $\log K_d$ is plotted against $\log[\text{F}^-]$ thus these curves can be expressed as:

$$\log K_d = a + b \log[\text{F}^-] + c \log[\text{F}^-]^2 \quad (1)$$

From which:

$$\left(\frac{\partial \log K_d}{\partial \log[\text{F}^-]} \right) = b + 2c \log[\text{F}^-] \quad (2)$$

Let us consider that the predominant species in solutions are: $[\text{Zr}(\text{Hf})\text{F}_6]^{2-}$, $[\text{Pa}(\text{Ta})\text{F}_7]^{2-}$ and for niobium $[\text{NbOF}_5]^{2-}$, thus the coefficients of ligand "j" were taken as $j = 5$ for Nb, $j = 6$ for Hf and Zr and $j = 7$ for Ta and Pa [1,9,14-17]. Thus, the $\delta \log K_d / \delta \log[\text{F}^-]$ values at different F^- ion concentration (1×10^{-3} to 3M) were determined for each pH, and the average F^- number "δ" in solution was obtained by equation 22 (see section 4.4) as a function of F^- ion concentration. Finally, the values of complex stability constants " k_j " were calculated by equation 21 (see section 4.4) using the method of "least squares".

In expression 21, anionic species only are presumed to be taken up by the anionic exchanger resin (the invasion of positive charged ions is negligible), in consequence only the formation of the first five anionic complexes have to be con-

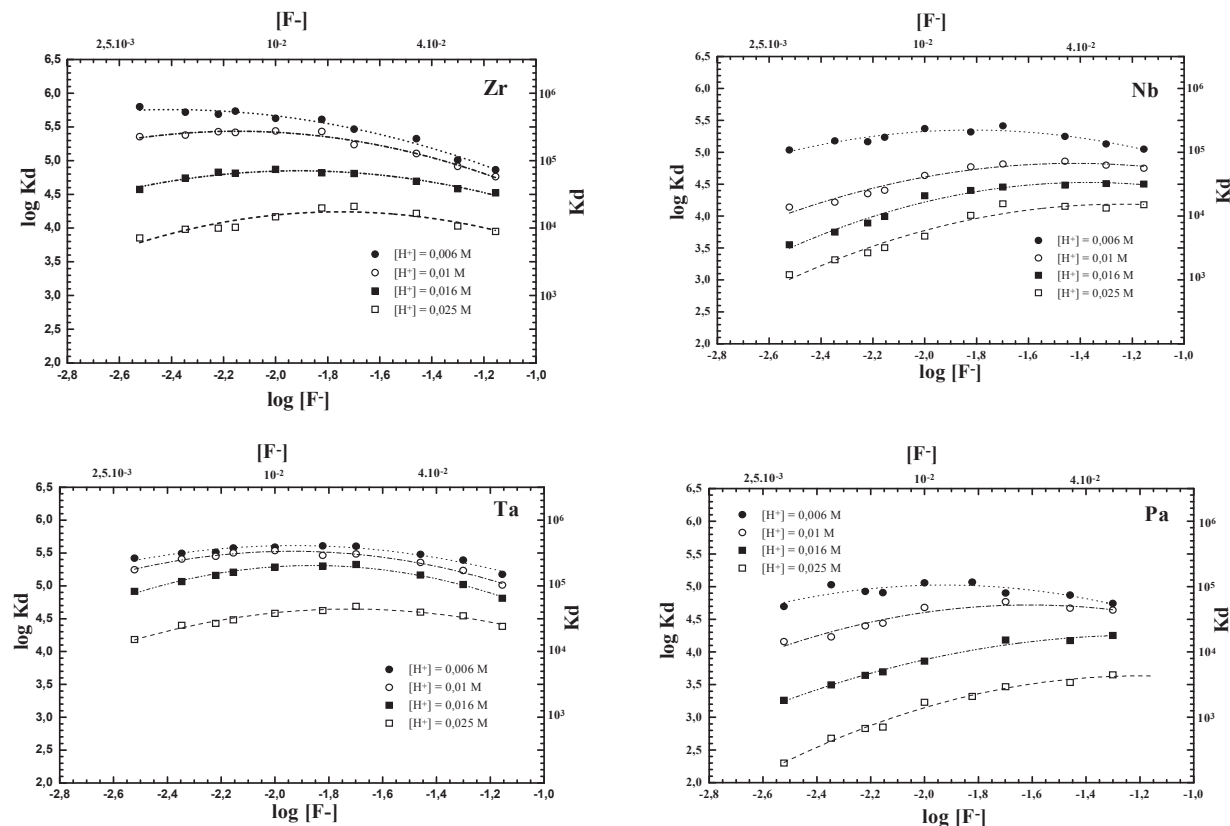


Fig. 2. Variation of Logarithmic K_d values as a function of $\log [F^-]$ at a pH constant for Zr, Nb, Ta and Pa. K_d values given in g/cm^3 .

sidered for Zr, Hf, Ta and Pa: $[MF_6]^-$ – $[MF_9]^{4-}$ and for niobium $[NbOF_4]^-$ – $[NbOF_9]^{4-}$ and $[NbF_6]^-$. Equation 21 could therefore be calculated for example, for Zr(Hf) as:

$$\bar{j} = \frac{4 + 5k_5[F^-] + 6k_6[F^-]^2 + 7k_7[F^-]^3 + 8k_8[F^-]^4 + 9k_9[F^-]^5}{1 + k_5[F^-] + k_6[F^-]^2 + k_7[F^-]^3 + k_8[F^-]^4 + k_9[F^-]^5} \quad (3)$$

The stability constants of fluoride complexing for all elements are presented in Table 1. These stability constants are a function of effects: 1) electrostatics: charge and radius of metal ion and ligand, 2) geometrics: radius of metal ion and sizes of the ligand, 3) statistical: the probabilities of $[MF_j]^{n-j}$ formation and dissociation, and 4) of pH in solution.

The repulsion or attraction depends upon the distance between the centres of the particles, being greater as the particles approach one to another. In consequence, the greater the charge on the ions, the greater should be the stability. Small ions are favoured because their centres can be closer together. From this point of view the stability of complexes should increase with the charge on the metal ions. In our case, the stability constants should be decrease in the order: M^{5+} (Nb, Ta and Pa) > M^{4+} (Zr and Hf). With respect to the stability of complexes of metal ions having the same charge should increase as the ionic radius decrease. In this case, the stability constant should decrease in the order: $Nb^{5+} > Ta^{5+} >$

$Pa^{5+} > Zr^{4+} > Hf^{4+}$. However this type of correlation differs sometimes from the experimental values. For example, the predominance species of Nb and Ta have the greater stability constant, but in the case of Pa, Zr and Hf, these values are not very different. At pH = 1.6 the $\log k_x$ values are for Nb $\log k_4 = 4.6$, for Ta $\log k_6 = 4.116$, for Pa $\log k_6 = 3.037$ and for Zr and Hf $\log k_5 = 2.8$ while at pH=2.2 the values are: 3.8, 3.4, 2.3, 2.8 and 0.5 respectively. The reason is not clear, therefore the fluoro complexes consist of several atoms, and it is difficult to assign a meaningful ligand radius and hence apply size criterion. It might also be due to covalence effects in the metal-ligand bonds.

The geometry of metal complexes is determined by the requirements: 1) to group the ligands (F^-) near the metal to minimize electrostatic repulsions and 2) to allow overlap of the metal and ligand orbitals. The large radius of atoms and ions in Periods 4 and 5 favour higher coordination number in the complexes that these elements form. The larger central atom permits the close approach of more than six ligands.

Distribution Diagrams of Fluoride Complexes

It is necessary to know the effect that the pH will have on the composition of each $[MF_j]^{(n-j)}$ species in solution. One easy way to see this effect is in terms of the relative concentra-

Table 1. Metal stability constants for complexes MF_x^{n-x} of cations Zr^{4+} , Hf^{4+} , Ta^{5+} , Pa^{5+} and oxo - complexes $NbO_xF_y^{5-(x+y)}$. Results valid for $3 \times 10^{-3} M < HF < 0.05 M$ and $[H^+] = 0.05, 0.12, 0.23$ and $0.4 M$, obtained on anionic exchanger.

$[H^+] M$	$\log K_4$	$\log K_5$	$\log K_6$	$\log K_7$	$\log K_8$	$\log K_9$
Zr						
0.006	-	1.53 ± 0.08	4.22 ± 0.17	1.78 ± 0.08	1.28 ± 0.05	-
0.01	-	2.44 ± 0.12	3 ± 0.12	1.53 ± 0.07	1.38 ± 0.05	-
0.016	-	2.98 ± 0.15	2.35 ± 0.09	1.48 ± 0.07	0.85 ± 0.03	-
0.025	-	2.55 ± 0.13	2.19 ± 0.09	1.32 ± 0.06	0.96 ± 0.04	-
Hf						
0.006	-	0.48 ± 0.02	5.02 ± 0.20	1.38 ± 0.06	1.78 ± 0.07	-
0.01	-	2.94 ± 0.15	2.86 ± 0.11	1.70 ± 0.08	1.11 ± 0.04	-
0.016	-	2.56 ± 0.13	2.31 ± 0.09	1.36 ± 0.06	1.14 ± 0.04	-
0.025	-	2.33 ± 0.12	2.17 ± 0.09	1.26 ± 0.06	1.04 ± 0.04	-
Ta						
0.006	-	-	2.96 ± 0.13	2.38 ± 0.13	1.49 ± 0.06	0.89 ± 0.04
0.01	-	-	2.5 ± 0.11	2.52 ± 0.13	1.37 ± 0.05	1.32 ± 0.07
0.016	-	-	1.9 ± 0.09	2.79 ± 0.15	0.96 ± 0.04	1.77 ± 0.09
0.025	-	-	2.6 ± 0.12	2.14 ± 0.11	1.31 ± 0.05	0.8 ± 0.04
Pa						
0.006	-	-	2.65 ± 0.12	2.43 ± 0.13	1.4 ± 0.05	1.17 ± 0.06
0.01	-	-	2.4 ± 0.11	2.04 ± 0.11	1.2 ± 0.04	0.8 ± 0.04
0.016	-	-	4.43 ± 0.20	1.65 ± 0.09	0.7 ± 0.03	-
0.025	-	-	1.73 ± 0.08	1.9 ± 0.10	-	1.6 ± 0.08
Nb						
0.006	-	0.95 ± 0.04	2.59 ± 0.10	-	-	-
0.01	2.59 ± 0.07	1.17 ± 0.05	1.23 ± 0.05	-	-	-
0.016	2.12 ± 0.07	1.61 ± 0.06	1.27 ± 0.05	-	-	-
0.025	2.1 ± 0.07	1.62 ± 0.06	1 ± 0.04	-	-	-

tions of the various possible species in solution which can be expressed by the equilibrium constant k_j and the concentration of $[F^-]$.

The relative concentration of each complexes $[MF_j]^{(n-j)}$ was found from:

$$\frac{[MF_j]^{n-j}}{[M^{n+}]_T} = \frac{k_j [F^-]^m}{1 + \sum_{j=0}^m k_j [F^-]^m} \quad (4)$$

The concentration of $[M^{n+}]_T$ corresponding to total concentration of $[M^{n+}]$ metal ion in solution, and " k_j " to complexing constants. This relationship is independent of the amount of metal $[M^{n+}]$ in the solution and the sum of the fractions must equal unity. The mole fraction of each metal species as a function of the F^- concentration were used to construct the distribution species plot of all elements at pH constant, which are show in Fig. 3-Fig. 6. The $[M^{n+}]^{0,x+}$ term, included in distribution diagrams represents all neutral and positive species which are not determined by this method.

The shape of these curves is determined by two parameters: i) the F^- ion concentration and ii) the pH. The pH causes the displacement of distribution curves toward low F^- concentration in proportion as pH increase; and higher ligand (F^-) numbers appear in the complexes as F^- concentration increases.

The complexation studies done are discussed individually, followed by a comparison of one with another.

A comparison of the Zr diagrams with those of Hf shows that the shapes of these curves are very similar. In aqueous solution (1×10^{-3} -1 M F^-), Zr(Hf) forms four anionic complexes: $[Zr(Hf)F_5]^-$, $[Zr(Hf)F_6]^{2-}$, $[Zr(Hf)F_7]^{3-}$ and $[Zr(Hf)F_8]^{4-}$. An increase in the concentration of F^- in the mixture, increases the number of ligands in the complexes. Thus in 3×10^{-3} M $[F^-]$ at pH 1.6 the complex $[Zr(Hf)F_7]^{3-}$ appears, $[Zr(Hf)]^{0,x+}$ begin to disappear and $[Zr(Hf)F_5]^-$ and $[Zr(Hf)F_6]^{2-}$ are present in 60 % and 25 % respectively, while to 1×10^{-1} M F^- at same pH, the species $[Zr(Hf)F_5]^-$ disappear and $[Zr(Hf)F_6]^{2-}$, $[Zr(Hf)F_7]^{3-}$ and $[Zr(Hf)F_8]^{4-}$ are present in 25 %, 40 % and 25 %, respectively. With respect to acidity effect, an increase in pH causes the formation of fluoro complexes containing an upper number of ligands $[F^-]$ in their structure. For example,

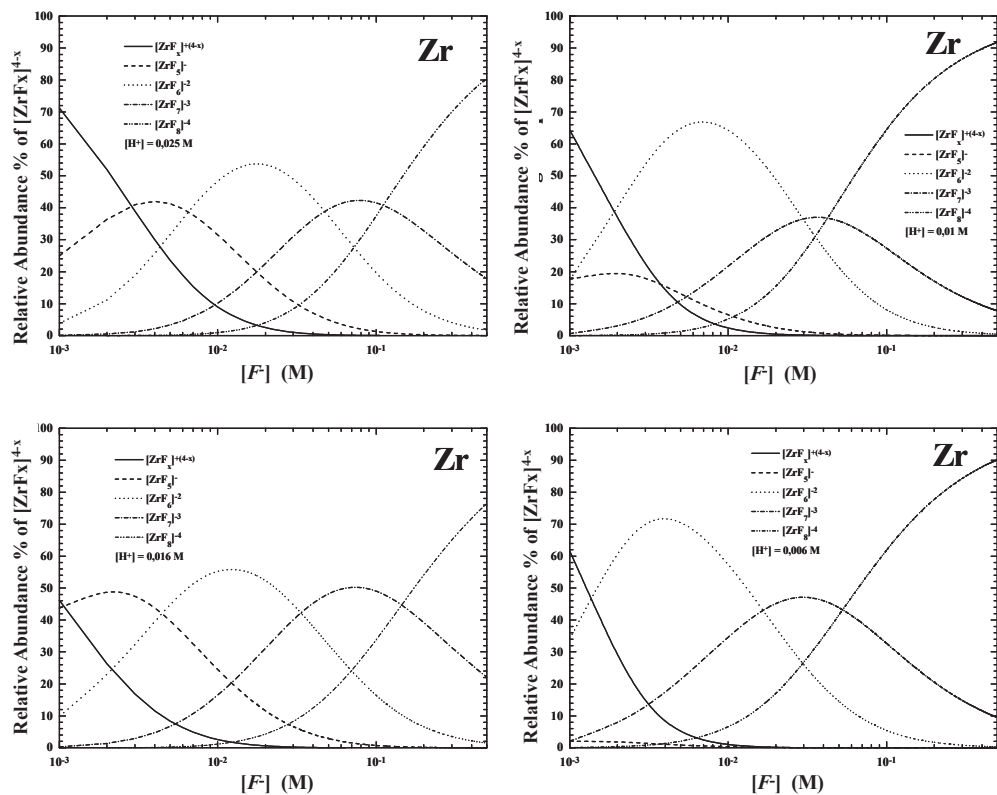


Fig. 3. Distribution diagrams of species at pH constant for Zr (Hf).

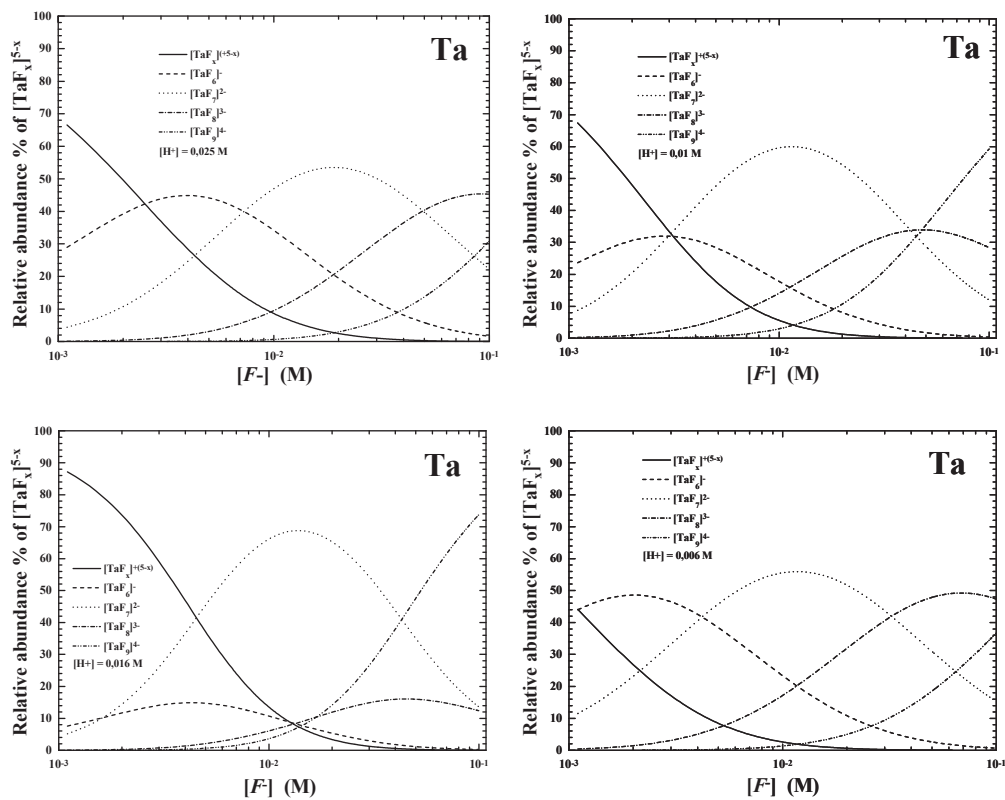


Fig. 4. Distribution diagrams of species at pH constant for Ta.

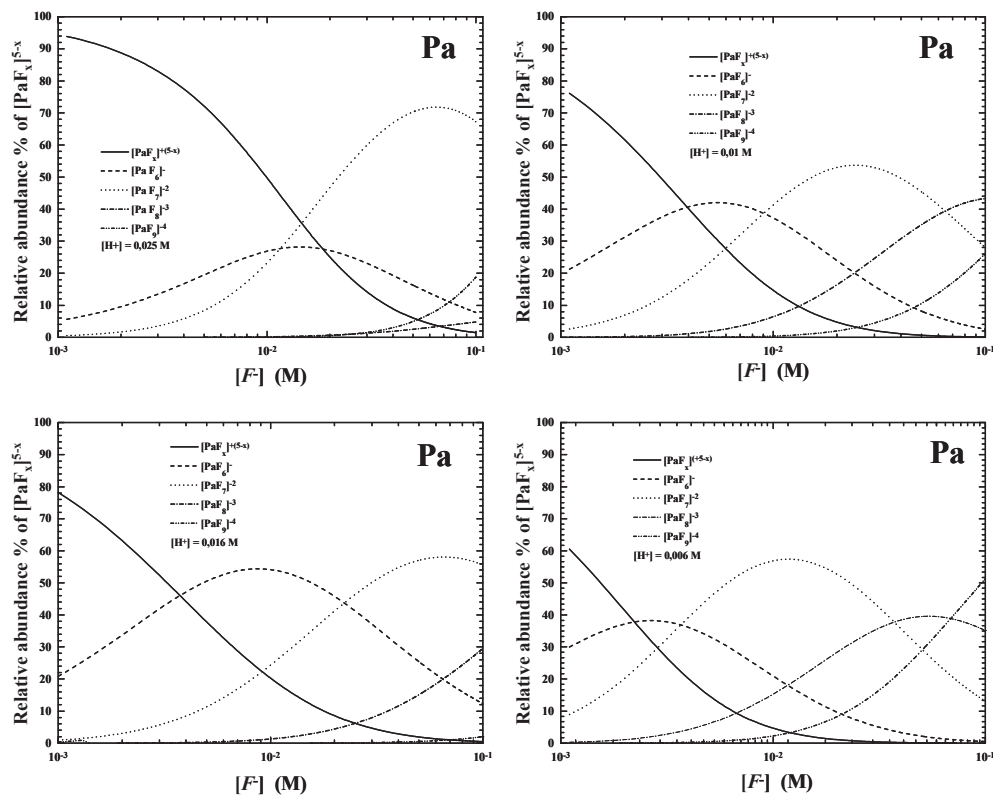


Fig. 5. Distribution diagrams of species at pH constant for Pa.

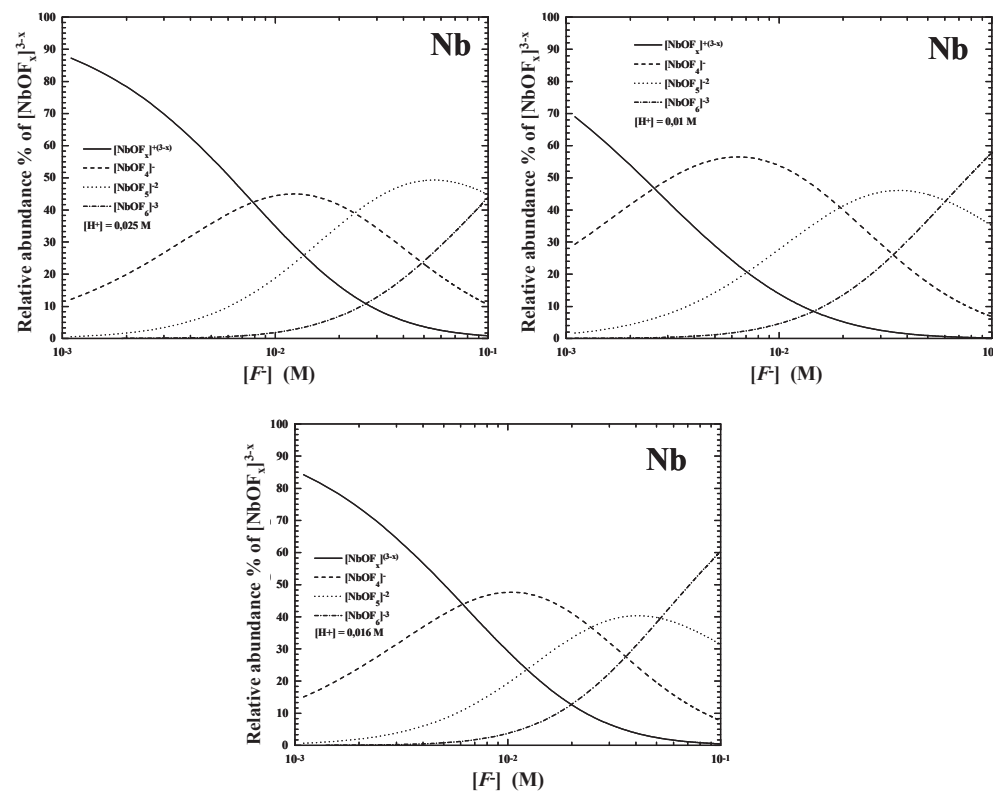


Fig. 6. Distribution diagrams of species at pH constant for Nb.

to 1×10^{-2} M F^- at pH = 1.6 the species $[Zr(Hf)F_5]^-$ (35%), $[Zr(Hf)F_6]^{2-}$ (55%) and $[Zr(Hf)F_7]^{3-}$ (10%) are present in solution, while at pH = 2.2 $[Zr(Hf)F_8]^{4-}$ complex appears in solution, $[Zr(Hf)F_5]^-$ begin to disappear and $[Zr(Hf)F_6]^{2-}$ and $[Zr(Hf)F_7]^{3-}$ represent 40% mole fraction. Similar trends were obtained for Ta, Pa and Nb. However, there are differences in the distribution of species which varies according to the nature of metal ion, the stability of fluoro complexes, the pH and the F^- concentration.

As shown in Fig 4, four types of complexes can mainly be formed in the solution containing Ta^{5+} and F^- : $[TaF_6]^-$, $[TaF_7]^{2-}$, $[TaF_8]^{3-}$ and $[TaF_8]^{4-}$. In the case of Pa^{5+} (Fig. 5), the predominant species are: $[PaF_6]^-$, $[PaF_7]^{2-}$, and $[PaF_8]^{3-}$, and for Nb (See Fig. 6): $[NbOF_4]^-$, $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ or $[NbF_6]^-$. It must recall, that these experiments give not information on complex charge, only the complex order (the number of $[F^-]$ ligands in the complex) can be measured without ambiguity. Obviously it is impossible to distinguish among species having the same number of $[F^-]$ ligands which include any other(s) "X" ligands in the same complex. For example, the mononegative complexes which can be formed from fluoride ion and Nb^{5+} aqueous ion may be written: $[NbOF_6]^{3-}$ or $[NbF_6]^-$. In this case, the reported mole fraction in Fig. 6 is the sum of two complex species: $[NbOF_6]^{3-}$ and $[NbF_6]^-$.

Distribution $[MF_j]^{(n-j)}$ species in HF solutions

The effect of several pH values on the formation of Zr, Hf, Nb, Ta and Pa fluoro complexes in $NH_4F/HClO_4$ system were shown previously. In these cases, the experimental results were analyzed considering the formation of these complexes at pH constant, because the formation of metal complexes is largely dependant on the F^- and H^+ concentrations which vary independently their concentrations, as shown in Fig. 7. Thus, it is possible to predict HF concentra-

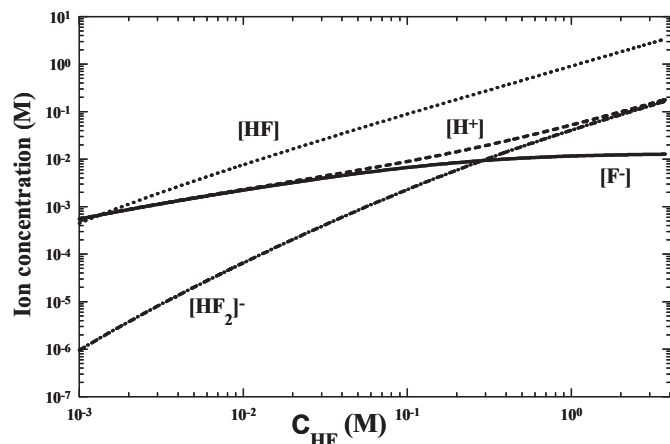


Fig. 7. The evolution of $[F^-]$, $[H^+]$, $[HF]$ and $[HF_2^-]$ as a function of initial $[HF]$. [12]

tion initial as a function of F^- and H^+ experimental ion concentration, to establish the causes of the slop break of $\log K_d$ vs. $\log [HF]$ (See Fig. 1).

In the HF range studied (2×10^{-2} to 4×10^{-1} M HF), the predominance of $[MF_j]^{(n-j)}$ species as a function of HF concentration, for Zr, Hf, Nb, Ta and Pa are shown in figures 3-6. In all cases, the variation of species distribution presents inflections to 0.12 M HF for Zr and Pa; and at 0.23 M HF for Nb and Ta. Accordingly, it was assumed that these inflections explain the decrease of the absorption properties as well as the slop break of $\log K_d$ vs. $\log [HF]$ (See Fig. 1).

In the case of the Hf(Zr), the relative concentration variation of the $[Zr(Hf)F_5]^-$, $[Zr(Hf)F_6]^{2-}$ and $[Zr(Hf)F_7]^{3-}$ species on and after 0.12 M HF causes mainly the slop break in $\log K_d$ vs. $\log [F^-]$. Thus, the adsorption (K_d) becomes smaller with the increase in HF content. In this connection, it is interesting to note the fact that the $[Zr(Hf)F_6]^{2-}$ and $[Zr(Hf)F_7]^{3-}$ species are converted to $[Zr(Hf)F_5]^-$ principally. Similar, but more pronounced tendencies were observed with Nb, Ta and Pa. $[PaF_7]^{2-}$ species is converted principally to $[PaF_6]^-$, $[TaF_6]^-$ to $[TaF_7]^{2-}$ and the $[NbOF_4]^-$ complex to $[NbOF_5]^{2-}$. This suggests that the mechanism of formation and dissociation of complexes, in these cases it is the same for all these elements.

The fluoride complex formation has been the subject for a number of investigations. A comparison of the results, obtained from several works referred to, is given in Table 2.

The k_j values found in the present work are higher or lower than those found by the other authors. This may be attributed to the different media used in each case.

Conclusion

The complex formation depends on many parameters, such as equilibrium constants, concentrations, solvation, etc., and particular conditions of an experiment.

Table 2. Fluoro-complexes of Zr(IV), Hf(IV), Nb(V), Ta(V) and Pa(V) at specific $[HF]$.

HF $\leq 10^{-2}$ M	10^{-2} M < HF < 3 M	HF ≥ 3 M
hydrolysis species positive and neutral $[Zr(Hf)OH_xF_y]^{4-(x+y)}$	fluoro complexes $[Zr(Hf)F_x]^{4-x}$ $4 \leq x \leq 6$	fluoro complexes $Hf(Zr)F_7^{3-}$ and $Hf(Zr)F_8^{4-}$
hydrolysis species Ta(Pa)Ox $F_y^{5-(x+y)}$ positive and neutral Ta(Pa) $F_y^{5-(x+y)}$	fluoro complexes $[Ta(Pa)F_x]^{5-x}$ $5 \leq x \leq 7$	fluoro complexes Ta(Pa) F_8^{3-} and Ta(Pa) F_9^{4-}
HF < 11 M		HF > 11 M
hydrolysis species $NbOF_5^{2-}$		fluoro complexes NbF_6^- and NbF_7^{2-}

The sorption behaviour of Zr, Hf, Nb, Ta and Pa on anion exchange in HF medium can be explained by the repartition of the complex populations in solution. The anionic complexes: $[\text{Zr}(\text{Hf})\text{F}_5]^-$, $[\text{Zr}(\text{Hf})\text{F}_6]^{2-}$, $[\text{Zr}(\text{Hf})\text{F}_7]^{3-}$, $[\text{Ta}(\text{Pa})\text{F}_6]^-$, $[\text{Ta}(\text{Pa})\text{F}_7]^{2-}$, $[\text{Ta}(\text{Pa})\text{F}_8]^{3-}$, $[\text{NbOF}_4]^-$ and $[\text{NbOF}_5]^{2-}$ are present as predominant species in the HF range investigated.

This method gives no information about the stability constants of cationic species, and finally, it should be emphasised that the values of $\log k_j$ in Table 1 are only applicable to specific conditions of pH, ionic strength and HF concentration.

Experimental

Tracer solutions

The ion exchange behaviour of Zr, Hf, Nb, Ta and Pa in fluoride medium was studied using the radioactive tracer listed in Table 3, which also shows the half-life and the main gamma-lines measured for each radioisotope.

Radioisotopes of Zr, Nb and Pa

The radionuclides ^{230}Pa , ^{95}Zr and ^{95}Nb were produced from $^{232}\text{ThO}_2$ [10] which was irradiated at the isochronous cyclotron of Orléans (CERI, France) with a 34 MeV proton beam of an intensity of 20 μA about 50 hours. The irradiated thorium target (around 30 g) was first dissolved in concentrated HCl. Due to the high radioactivity of the target (about 0.5 Gy at close contact); all the first separations were done semi-automatically in a shielded glove box. The medium was then fixed to 10 M HCl by adding water. The resulting solution was percolated on an anion exchanger column filled with Dowex 1GX8, pretreated with 10 M HCl. In this medium, Th is not retained, while Pa, U, Zr and Nb and most of the other fission products (Sb, Ru, etc.) remain held in the column. A selective elution of Pa, Zr and Nb was then conducted using a 10 M HCl and 0.05 M HF [9]. Finally, the last purification was done by separating Pa, Zr and Nb from the other residual fission products (mainly ^{103}Ru and ^{125}Sb), on a small anionic exchanger. The solution was evaporated near dryness and the medium was changed to 0.2 M HF and percolated on the column. In this

medium, Pa, U, Zr and Nb are quantitatively retained with large distribution coefficients ($K_d > 10^5$). Washing with 2 M HF allowed desorbing of the residual contaminants. The elution was then conducted using 1 M HCl. The elution process is very fast and 2 cm^3 were enough to recover Pa, Zr and Nb fraction. The medium was then changed, after evaporation, to 0.5 M HF, and this solution of high specific activity was stored as stock solution (about 0.1 to 0.2 $\mu\text{Ci}/\mu\text{L}$ for each element) [9].

Radioisotopes of Hf and Ta

The $^{175,181}\text{Hf}$ and ^{182}Ta radioisotopes were obtained from neutron irradiated hafnium oxide and metallic tantalum, respectively. In order to obtain a solution of high specific activity, the irradiation was conducted over 72 hours under a neutron flux of about 10^{14} neutrons $\text{s}^{-1} \text{cm}^{-2}$. After a sufficient decay time, the irradiated samples were dissolved in concentrated HCl, evaporated and then stored as a 0.5 M HF stock solution [9].

K_d determination

Chemical reagents used were all of analytical grade. The ion exchange resin used was the strong basic macroporous anion exchanger BIORAD AGMPI (analytical grade 200-400 mesh, Cl^- form). After washing with distilled water the resin was dried at 70°C for 24 h. Solutions of $\text{NH}_4\text{F}/\text{HClO}_4$ were prepared by adding 70-72 % HClO_4 ($\delta = 1.67$) to 0.1 M NH_4F solutions and adjusting to a definite volume with distilled water. All materials in contact with HF solutions were inert (in Teflon or polyethylene).

The distribution ratio K_d is defined as the ratio of the total (analytical) amount of a species per gram of dry resin to total amount per mL of solution and was determined by the batch equilibration technique. For this purpose, 100 to 50 μL of the stock solutions, containing the tracer elements, were mixed with: 50 to 100 mg of the resin (m_{res}), and ammonium fluoride-perchloric acid mixed solutions adjusted to 5 mL with distilled water (V_{sol}). Equilibrium between the aqueous phase and the resin was attained by mechanical shaking for 24 h in polyethylene vials. After equilibration, the resin and the liquid phase were separated by centrifugation and filtration through microfilters of 0.2 μm . Standards were prepared from solutions containing the same amount of the stock solutions in 4 cm^3 $\text{NH}_4\text{F}/\text{HClO}_4$ mixed. The concentration of the metal ions varied from traces to about 10^{-10} M for Pa, Zr and Nb and less than 10^{-7} M for Hf and Ta.

Resin adsorption was determined by comparing the activity of a 4 mL aliquot of this filtrate (A_{sol}) with that of 4 mL aliquots of standards solutions (A_{stand}). The K_d values were calculated by means of the following expression:

$$K_d = \frac{\text{activity per gram of resin}}{\text{activity per milliliter of solution}} = \left(\frac{A_{\text{stand}} - A_{\text{sol}}}{A_{\text{sol}}} \right) \cdot \frac{V_{\text{sol}}}{m_{\text{res}}} \quad (5)$$

Table 3. Main decaying characteristics of the radioisotopes studied.

Radionuclide	Half-life (days)	Gamma lines (keV)
Zr-95	64.4	724.2 756.7
Nb-95	35.2	765.8
Hf-181	42.5	133.1 482.2
Ta-182	115	1121.3 1221.4
Pa-230	17.4	443.8 918.5 952.0

All measurements of the radioactivity were carried with a coaxial gamma detector GeHP of 40 % efficiency with an energy resolution of 1.75 KeV for the 1.332 MeV ^{60}Co peak, connected to a multicannal analyzer to the same geometrical conditions. Thus corrections due to decay during the measure times (about 24 h) were applied on the necessary cases. All tests were carried out in duplicate and the average of the duplicate results is reported.

Ion exchange equilibrium

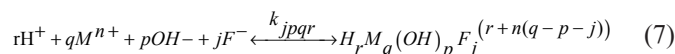
By means of the ion exchange equilibrium, the partition of elements is characterized by a distribution coefficient $D = C_M/C_M$ (generally in equilibrium) where C_M and C_M are the metal ion concentration in the aqueous and solid phase, respectively (both being proportional to their radioactivity). D may be a complex function of C_M , C_M , and k_j (and other constants) and the equilibrium concentration $[F^-]$ of the two phases of the system. If the distribution coefficients are related to a unit weight of the exchanger and to a unit volume of the solution, it is denoted by " K_d " [12]. Examination of the function $K_d = f([F^-])$ (C_M or $C_M = \text{constant}$) reveals that $\log K_d / \log [F^-]$ always equals the difference between the average stoichiometry coefficients of the various species formed in each phase [4,13]. In the case of the ligand $[F^-]$:

$$\frac{\delta \log K_d}{\delta \log [F^-]} = \langle j \rangle - \langle \bar{j} \rangle \quad (6)$$

Where j is the number of ligands necessary to form the complex in the resin and aqueous phase [4,6]. However, the variations in K_d versus $[F^-]$ do not give enough information to characterize the species and consequently to obtain k_j . Nevertheless it is possible to choose experimental conditions which produce a simpler K_d function, for example: when only monomeric species exist in both phases, K_d is only a function of the parameters $[F^-]$ and of the constants such as k_j , which relate to complex species. And if the consumption of macroscopic reagent is negligibly small then it is possible to consider the analytical concentration approximates concentration $[F^-] = C_F$ and $K_d = f([F^-] = C_F)$ [4].

Determination of complex stability constants k_j

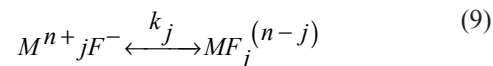
The following scheme shows the reactions between a metal ion M^{n+} and ligand F^- in a complex system:



Where M^{n+} can be: Zr^{4+} , Hf^{4+} , Nb^{5+} , Ta^{5+} and Pa^{5+} . The equilibrium constant of reaction 7 is given as:

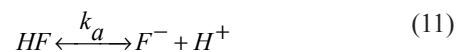
$$k_{jpqr} = \frac{[H_r M_q (OH)_p F_j^{(r+n(q-p-j))}]}{[H^+]^r [M^{n+}]^q [OH^-]^p [F^-]^j} \quad (8)$$

Under conditions of homogeneity (low concentrations of the components) hydroxo-complexes are not formed and $r = 0$, $p = 0$. An absence of polymers can be assumed for all elements when $C_M < 10^{-7}$ M and concentrations are easily detectable with the use of short half-life tracers ($q = 0$) [6] then the complex equilibrium in the fluoride system can be represented by the equations:

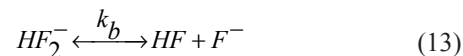


$$k_j = \frac{[MF_j^{(n-j)}]}{[M^{n+}][F^-]^j} \quad (10)$$

In this equation F^- is a definite (assumed to be predominant) form produced by the dissociation of the HF which is characterised by the consecutives dissociation constants: k_a and k_b :



$$k_a = \frac{[F^-][H^+]}{[HF]} = 6.7 \times 10^{-4} \quad (12)$$



$$k_b = \frac{[HF][F^-]}{[HF_2^-]} = 0.25 \quad (14)$$

The evolution of these species as a function of initial HF concentration is shown in figure 7. The total concentrations of M^{n+} (species) C_M and F^- (species) C_F in the solution, whether they are complexed or not [14], are given by:

$$C_M = [M^{n+}] + \sum_{j=1} MF_j \quad (15)$$

$$C_F = [F^-]_T + \sum_{j=1} jMF_j \quad (16)$$

where $[F^-]_T$ is the total concentration of fluoride ions in solution, not combined in the complex [14], in the system:

$$[F^-]_T = [F^-] + [HF] + 2[HF_2^-] \quad (17)$$

The equations (15) and (16) can be rewritten using the stability constants k_j :

$$C_M = [M^{n+}] + \sum_{j=1} k_j [F^-]^j \quad (18)$$

$$C_F = [F^-]_T + \sum_{j=1} j k_j [F^-]^j \quad (19)$$

The distribution ratio \bar{j} , also defined as average ligand number, of the total concentration of F^- (C_F) and the total concentration of fluoride ions in solutions $[F^-]_T$ between the difference of the total concentration of M^{n+} (C_M) can be expressed as follows:

$$\bar{j} = \frac{C_F - [F^-]_T}{C_M} \quad (20)$$

On combining the equations 18 and 19, and rearranging, we obtain:

$$\bar{j} = \frac{\sum_{j=1} j k_j [F^-]^j}{1 + \sum_{j=1} k_j [F^-]^j} \quad (21)$$

The average ligand number \bar{j} in the solution is obtained from the expression:

$$\bar{j} = j - \left(\frac{\partial \log k_d}{\partial \log [F^-]} \right)_{pH=cte} \quad (22)$$

Where j is based on the assumption that ligand number of the species sorbed by the resin is known, and $\delta \log K_d / \delta \log [F^-]$ is obtained from the experimental data of the variation of $\log K_d$ with $[F^-]$ at constant pH and the k_j stability constants are calculated using the least squares computer methods [6].

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