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ANION EXCHANGE BEHAVIOR OF Ti, Zr, Hf, Nb
AND Ta AS HOMOLOGUES OF Rf AND Db IN MIXED
HF-ACETONE SOLUTIONS

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Анионообменное поведение Ti, Zr, Hf, Nb и Ta как гомологов Rf и Db в смешанных растворах HF-ацетон

Исследована сорбция Ti, Zr, Hf, Nb и Ta как гомологов Rf и Db анионом AG 1 из смешанных водно-органических растворов HF-ацетон в зависимости от концентрации кислоты и ацетона. Обнаружено, что на анионообменное поведение сильно влияет концентрация ацетона. Коэффициенты распределения Ti, Zr, Hf и Nb на анионите увеличиваются с увеличением концентрации ацетона в растворах HF, а Ta — уменьшаются. Анализ анионообменного равновесия показал, что с увеличением концентрации HF предпочтительнее сорбируются анионные фторидные комплексы элементов 4-й группы с зарядом -3 , Ta — -2 . Для Nb заряд -2 увеличивается с увеличением концентрации ацетона до -5 . Найдены оптимальные условия для разделения исследованных элементов методом анионообменной хроматографии. В условиях эксперимента элементы 4-й группы предположительно образуют комплексы MF_7^{3-} ($M = \text{Ti, Zr, Hf}$), сорбция которых уменьшается в ряду $\text{Ti} > \text{Hf} > \text{Zr}$ в обратной последовательности устойчивости комплексов. Это показывает, что особый интерес будет представлять изучение ионообменного поведения Rf в сравнении с Ti. Обсуждаются преимущества изучения химических свойств Rf и Db в водно-органических растворах HF.

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Anion Exchange Behavior of Ti, Zr, Hf, Nb and Ta as Homologues of Rf and Db in Mixed HF-Acetone Solutions

We studied in detail the sorption behavior of Ti, Zr, Hf, Nb and Ta on AG 1 anion exchange resin in HF-acetone mixed solutions as a function of organic cosolvent and acid concentrations. Anion exchange behavior was found to be strongly acetone concentration dependent. The distribution coefficients of Ti, Zr, Hf and Nb increased and those of Ta decreased with increasing content of acetone in HF solutions. With increasing HF concentration, anion exchange equilibrium analysis indicated the formation of fluoride complexes of group-4 elements with charge -3 and Ta with charge -2 . For Nb the slope of -2 increased up to -5 . Optimal conditions for separation of the elements using AIX chromatography were found. Group-4 elements formed MF_7^{3-} ($M = \text{Ti, Zr, Hf}$) complexes whose sorption decreased $\text{Ti} > \text{Hf} > \text{Zr}$ in reverse order of complex stability. This fact is of particular interest for studying ion exchange behavior of Rf compared to Ti. The advantages of studying chemical properties of Rf and Db in aqueous HF solutions mixed with organic solvents are briefly discussed.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR, and Dzhelapov Laboratory of Nuclear Problems, JINR.

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INTRODUCTION

Chemical identification of radionuclides in the decay chains of the recently discovered transactinide elements may serve as a method for confirming the discovery [1]. The longer half-lives of radionuclides of transactinides discovered in the $An + {}^{48}\text{Ca}$ reactions make possible the application of radiochemical techniques for their chemical characterization in solutions [2]. In previous experiments, an ion exchange method combined with Db fluoride complexation was used [3, 4]. It is well known that ion exchange in water-miscible organic solvents exhibits more effective separation of metal ions [5]. To optimize conditions for isolation and study of chemical properties of Rf and Db, we investigated anion exchange behavior of their lighter homologues in groups 4 and 5 respectively, from HF-acetone mixed solutions. In addition, the influence of organic cosolvent on fluoride complexation and behavior in concentrated HF solutions of these elements were also examined. The sorption behavior of Ti, Zr, Hf, Nb and Ta on AG 1 anion exchanger in aqueous-organic solutions of HF as a function of organic cosolvent and acid concentrations was studied in detail.

EXPERIMENTAL METHODS

All the chemical reagents used were of analytical grade. The concentration of the initial HF solution was checked by titration with freshly prepared standard KOH solutions. Anion exchange resin AG 1X8 (Cl^- form, 200–400 mesh) was purchased from Fluka Chemika. Prior to use, the resin was washed with distilled water and then converted to F^- form by washing with 2 M HF. After that the resin was air-dried in an oven at 60°C for 24 hours and samples of 100 mg each were weighed. HF-acetone mixed solutions were prepared by weighing required quantity of acetone to HF solutions and bringing to final volume with distilled water. The volume of the samples was 1 cm^3 of mixed solution.

We used radionuclides ${}^{44}\text{Ti}$, ${}^{88}\text{Zr}$, ${}^{181}\text{Hf}$, ${}^{92}\text{Nb}$ and ${}^{182}\text{Ta}$ which were produced at JINR facilities. ${}^{182}\text{Ta}$ and ${}^{181}\text{Hf}$ were obtained from neutron-irradiated metallic forms of ${}^{181}\text{Ta}$ and ${}^{180}\text{Hf}$ (IBR-2 FLNP). Irradiated targets of ${}^{181}\text{Ta}$ and ${}^{180}\text{Hf}$ were dissolved in mixed conc. HF–0.5 M HNO_3 and conc. HF solution, respectively. ${}^{88}\text{Zr}$ and ${}^{92}\text{Nb}$ prepared by irradiation of Sr and Y (natural isotope abundance) with α particles (initial energy 35 MeV, He^+ beam current $\sim 10\ \mu\text{A}$,

exposure time 4 hours) on U-200 accelerator (FLNR). Production and radiochemical purification of ^{88}Zr were performed as described in [6] and for ^{92}Nb by analogy with [7].

^{44}Ti was produced in spallation reactions of Cu. Irradiated metallic copper (660 MeV protons at the phasotron (DLNP)) was dissolved in conc. HNO_3 . 3 mg Fe in the form of a $\text{Fe}(\text{NO}_3)_3$ solution was added and the hydroxide precipitated with concentrated ammonia solution. Under these conditions ^{44}Ti coprecipitates and Cu and most of nuclear reactions products (Co, Ni, Zn) remain in solution. For separation of ^{44}Ti from Fe and radionuclides of Mn, Cr, V, Sc cation exchange chromatography in HCl solutions was used. The 1 ml stock solution, containing no carrier added ^{44}Ti , ^{88}Zr , ^{92}Nb and $10 \mu\text{g}\cdot\text{ml}^{-1}$ ^{180}Hf and ^{181}Ta each, was prepared with a 20 M HF.

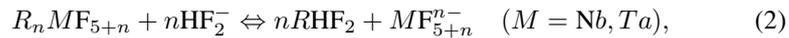
A series of batch experiments were performed at room temperature in order to determine distribution ratio of Ti, Zr, Hf, Nb and Ta between mixed HF-acetone solutions and AG 1 anion exchanger. In all experiments the solid to solution ratio was $10 \text{ cm}^3 \cdot \text{g}^{-1}$. Prepared solutions and resin were added into Eppendorf tubes and samples were left for 2 days in order to reach equilibrium. After that the samples were centrifuged for 10 minutes and aliquots from supernatant were taken. Amounts of element adsorbed onto resin were determined from the difference between radioactivity in solution before and after the equilibration time. Gamma-spectrometric determination of radionuclides was performed using a Ge detector from Ortec having energy resolution of 1.5 keV for the ^{60}Co γ -quantum energy at 1.33 MeV and coupled to a multichannel analyzer from Ortec.

Values of the distribution coefficient ($K_d, \text{ml} \cdot \text{g}^{-1}$) of Ti, Zr, Hf, Nb and Ta in AG 1 — HF-acetone mixed solutions system were published in [8].

RESULTS AND DISCUSSION

The obtained results let us make some conclusions about complexation and mechanism of sorption of group-4 and 5 elements in HF-acetone mixed solutions. The influence of acetone on sorption behavior of studied elements can be seen in Fig. 1.

Such behavior can be explained by two competing processes. It is known that in the concentrated HF solution formation of HF_2^- is predominant [9]. Thus, ion exchange equilibrium of fluoride complexes could be represented by the following chemical reactions:



where R is fixed ion group of the resin. In the presence of acetone, dissociation of HF decreases as the concentration of acetone increases because the dielectric

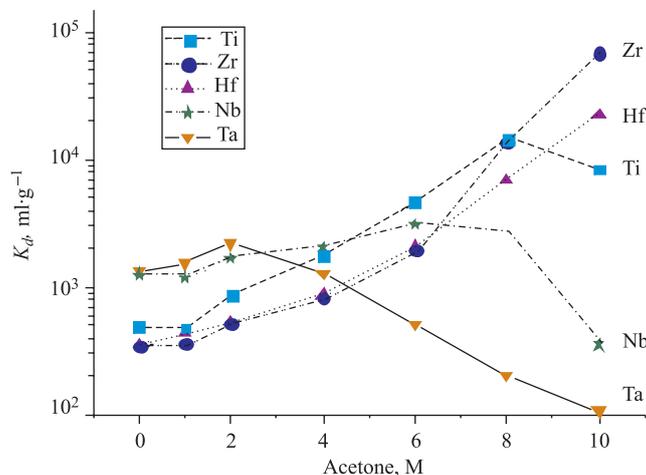


Fig. 1. K_d values of Ti, Zr, Hf, Nb and Ta as a function of acetone concentration for 6 M HF (AG 1X8, F⁻)

constant of acetone is higher than that of water. As a result, the concentration of counter ion HF₂⁻ decreases and sorption of fluoride complexes of Ti, Zr, Hf and Nb increases (Fig. 1). At acetone concentrations higher than 8 M for Nb, Ti and 10 M for Zr, formation of less negatively charged and neutral complexes takes place and sorption decreases. Influence of acetone on adsorption of Ta appears to be in the opposite direction. Effect of acetone on Ta uptake by AG 1 was found to be negligible within the interval 0–1 M. Further increasing of acetone concentration leads to a decrease in retention.

Effect of increasing HF concentration in mixed HF-acetone solution on the distribution of fluoride complexes was examined and results are presented in Fig. 2. Maximum K_d values of all the studied elements were found at HF concentration range between 0.1 and 1 M, indicating formation of strong fluoride complexes with F⁻ ions. Further increase of HF (> 2 M) concentration results in formation of the HF₂⁻ counter ion and shift of ion exchange equilibrium (Eqs. (1) and (2)). Consequently the sorption of Ti, Zr, Hf, Nb and Ta decreases at higher concentrations of HF due to displacement of anion complexes with the HF₂⁻ ion (Fig. 2).

According to anion exchange equilibrium (Eqs. (1) and (2)), K_d can be represented as follows:

$$\log K_d = \log D - n \log \frac{[\text{HF}_2^-]}{[\text{RHF}_2]}, \quad (3)$$

where D is the selectivity coefficient of exchanging anions, n is the number of charges of anionic complexes MF_{4+n}⁻ or MF_{5+n}⁻. Results of calculation of n are

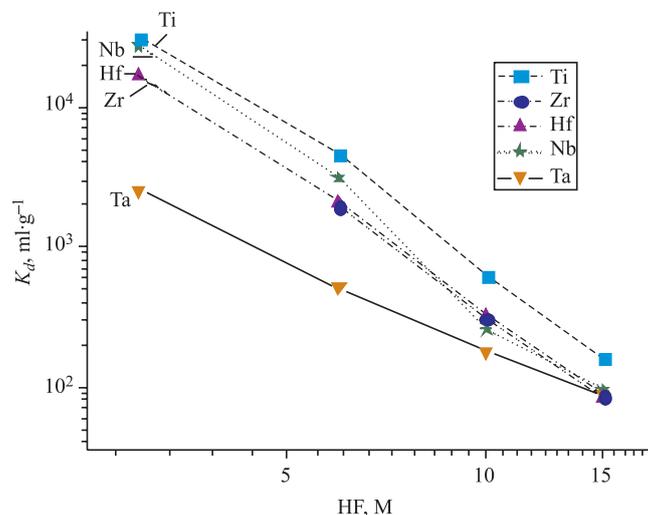


Fig. 2. K_d values of Ti, Zr, Hf, Nb and Ta as a function of HF concentration for 6 M acetone (AG 1X8, F⁻)

presented in Table 1. Since we do not know concentration of HF₂⁻ ions in acetone-containing solutions, values of n were calculated according to concentration of HF. Nevertheless, it can be seen that the values of n calculated from HF and HF₂⁻ in the absence of acetone are nearly equal. The values of n for Ti, Zr and Hf are approximately 3, while the values of n for Nb and Ta are approximately 2. It should be noted that with increasing acetone concentration the values of n for Ti, Zr, Hf and Ta increase a little and for Nb the value increases up to 5.

At low pH and in the presence of HF, group-4 elements are known to form anionic complexes MF_5^- , MF_6^{2-} , MF_7^{3-} ($M = Zr, Hf$) [5, 10]. Therefore, it can be concluded that under the present experimental conditions Ti, Zr and Hf exist in the form of MF_7^{3-} complexes. However, literature data indicates that in the presence of F⁻ ions the dominant species in the solution is MF_6^{2-} [10, 11]. We can assume

Table 1. Charges of anionic complexes of Ti, Zr, Hf, Nb and Ta in HF-acetone mixed solutions. Calculated from Eq. (3)

Acetone, M		Ti	Zr	Hf	Nb	Ta
0	HF ₂ ⁻	2.9	3.1	3.1	2	2
0	HF	3.1	3.2	3.1	2.1	2.1
1	HF	3.1	3.1	3.1	2.2	2.1
2	HF	3.2	3.1	3.2	2.3	2.2
4	HF	3.3	3.3	3.3	3	2.2
6	HF	3.3	3.4	3.3	3.7	2.1
8	HF				5.1	2.4

Table 2. Separation factors for the separation of Nb and Ta by anion exchange on the AG 1 in mixed HF-acetone solutions

HF, M	Acetone, M								
	0	1	2	4	6	8	10	12	13
0.5	—	—	—	—	—	—	—	> 14	> 24
1	—	—	—	—	—	> 6.5	> 28	> 51	3.2
3	1.5	2	1.5	3.8	11	17	> 450	4.1	
6	0.9	0.8	0.8	1.6	6.1	13	3.3		
10	0.6	0.6	0.6	0.9	1.5	1.3			
15	0.6	0.8	0.9	1.1	1.1				
20	1.4	1.4	1.4						
25	1.5	1.3							

that at high HF concentration MF_7^{3-} complexes become dominant species which preferentially adsorb on anion exchange resin and take part in sorption-desorption processes. Sorption of group-4 elements decreases Ti > Hf > Zr in reverse order of complex stability. This is in agreement with the previously reported data [6, 12] where, by using CIX chromatography and HCl-HF mixed solutions, group-4 elements were separated and eluted in the order Zr > Hf > Ti > Th according to fluoride complex stability constants. While in the absence of acetone, sorption of Ti, Zr and Hf was found to be equal, in the presence of acetone the selectivity and order of sorption on the resin changed dramatically (Fig. 1).

Retention of Nb and Ta in the presence of acetone is more complex. In the presence of fluoride the group-5 elements speciation is dominated by complexes NbF_6^- , $NbOF_5^{2-}$, TaF_6^- , TaF_7^{2-} existing at different concentration of F^- [13]. As shown in Fig. 1 and Table 1, in the absence of acetone Nb and Ta exist in the form of $NbOF_5^{2-}$ and TaF_7^{2-} , and their sorption decreases in the order of Nb > Ta. At acetone concentration higher than 2 M, anion exchange behavior of Ta becomes different from Nb, indicating formation of not adsorbed complexes. At the same time, the mean number of charges of Nb anionic complexes increases.

The data presented here are of great practical interest since conditions could be found for separation of all the studied elements. Table 2 shows separation factors for Nb and Ta over the range of HF and acetone concentrations studied. Optimal conditions for separation of group-4 elements from each other is 6 M HF – 10 M acetone and from group-5 elements is 15–25 M HF – 1–4 M acetone.

CONCLUSIONS

The results indicated that in concentrated (> 3 M) HF solutions containing acetone, group-4 elements formed complexes MF_7^{3-} ($M = Ti, Zr, Hf$) whose stability decreased in reverse order of sorption Zr > Hf > Ti. This fact is of particular interest for studying ion exchange behavior of Rf compared to Ti.

Under the same conditions, group-5 elements predominately formed complexes NbOF_5^{2-} and TaF_7^{2-} with anion exchange behavior considerably different in the presence of acetone. We found optimal conditions for separation of the elements using AIX chromatography.

Selectivity of sorption of all the studied elements in mixed solutions was found to be strongly acetone concentration dependent. This fact can be used for studying the influence of relativistic effects on complex formation of Rf and Db. Using mixed solutions with high concentration of acetone will decrease time for spectrometric samples preparation by evaporation of eluate in experiments with Rf and Db.

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