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Sorption Behaviour of Uranium on Cation and Anion Exchange Resins from HCl/HF-Containing Aqueous Solutions: Model Experiments for the Determination of Chemical Properties of Element 106 (Seaborgium)

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Summary

²³²U was used for batch studies of its sorption behaviour on DOWEX 50X8 and DOWEX 1X8 from diluted HCl/HF containing solution. It was shown that uranium remains, similar to subgroup IV elements, completely on the cation exchanger in the concentration range of 10^{-4} – 10^{-2} M HF and 10^{-2} –1.0 M HCl, whereas it is not at all sorbed on the anion exchanger. This behaviour differs completely from that of tungsten and molybdenum under similar conditions. With this chemical system it is possible to determine the chemical properties of element 106 (seaborgium) by comparing its sorption behaviour on the cation exchanger with that of tungsten, molybdenum, and uranium.

Introduction

Batch experiments with carrier-free isotopes of subgroup IV, V and VI elements showed that ion exchange on cation exchange resins (e.g. DOWEX 50WX8 or AMINEX A6) from diluted HCl/HF-containing solutions are applicable for fast on-line experiments aiming to separate seaborgium. The suitable concentration interval for the separation of the hexavalent elements tungsten and molybdenum from zirconium, hafnium and lanthanides was found to be 0.05–0.1 M HCl/ 10^{-4} – 10^{-3} M HF [1]. This chemical system was successfully applied in on-line experiments with short-lived tungsten, hafnium and lutetium isotopes [2].

On-line studies with ¹⁶⁵Hf and ¹⁶⁸W using the ARCA apparatus obtained similar results for HCl/HF and HNO₃/HF-containing solutions [3].

A first separation of seaborgium in aqueous solution with the ARCA III apparatus was carried out in 1995 at the UNILAC accelerator (GSI Darmstadt). In this experiment, 0.1 M HNO₃/ 5×10^{-4} M HF was used to adsorb element 104 and heavy actinides on the cation exchanger AMINEX A6. Two decay chains corresponding to the decay of ²⁶¹104 $\xrightarrow{\alpha}$ ²⁵⁷No $\xrightarrow{\alpha}$ were found in the aqueous phase. This clearly indicates that the 104 must come from the decay of seaborgium and is

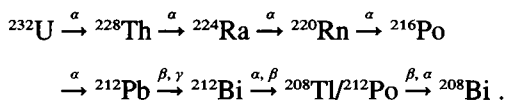
therefore proof for the presence of Sg in solution. Element 104 that was produced during the production of seaborgium also is expected to be completely adsorbed on the cation exchanger under these conditions. This result is a first proof that element 106 behaves like its lighter homolog tungsten in solutions containing HCl/HF or HNO₃/HF [4].

However, due to relativistic effects, similarities of the chemical properties of the transactinide elements with the corresponding actinides can also be expected. It was shown that element 105 has similar properties to subgroup V elements [5–7] but also behaves sometimes like Pa [8, 9]. Therefore, further chemical experiments with seaborgium should also consider the possibly uranium-like behaviour of this element. The sorption behaviour of carrier-free uranium from diluted HCl/HF or HNO₃/HF solutions used in the experiments that were described above is yet unknown. To compare the chemical properties of seaborgium with those of uranium, we investigated the sorption behaviour of ²³²U on cation and anion exchangers from HCl/HF solutions under the conditions used in [1]. Our present experiments were carried out in “batch” modus where the experimental time is rather long in comparison to the reaction time. This method ensures that chemical equilibrium is being reached between the element and its reaction partners in solution. A disadvantage of our batch experiments is that the reaction time cannot be decreased below 5 min. Fast on-line separations require only less than one minute. They have to be tested with model elements in order to establish whether or not the reaction reaches equilibrium before the fast separation is being carried out.

Experimental

Carrier-free ²³²U was obtained as a decay product of ²³²Pa (β^{-} , $T_{1/2} = 1.31$ a), which was produced via the nuclear reaction ²³²Th(p,n)²³²Pa(β^{-}) in 1976 at the Phasotron “F” (Laboratory for Nuclear Problems, JINR, Dubna, Russia). After the complete decay of ²³²Pa, a pure product was obtained which contained

only ^{232}U and its decay products. ^{232}U decays via the following decay chain:



^{228}Th and its daughter products were separated immediately before the experiments by sorbing the ^{232}U on DOWEX 1X8 from 9 M HCl solution. ^{228}Th passes through the column without sorption. The column was several times washed with 9 M HCl to remove all traces of thorium. ^{232}U was eluted from the column with 2 M HCl. This stock solution was diluted to the required HCl concentration as needed.

For the batch experiments, 5 mL of the radioactive solution were contacted for one hour with 200 mg of each ion exchange resin (DOWEX 50WX8, DOWEX 1X8, 20–50 mesh). Then the phases were separated. The distribution of ^{232}U was determined by evaporating 0.1 mL of the solution before and after the experiment and measuring the α -activity (^{232}U : $E_{\alpha} = 5139, 5263, 5329$ keV, all daughter products in the decay chain have higher α energies) using a Si(Au) detector (12 cm², resolution 35 keV).

The distribution coefficients were calculated as reported previously [1, 10].

Results and discussion

The suitable concentration interval of 0.05–0.1 M HCl/ 10^{-4} – 10^{-3} M HF for the separation of subgroup VI from subgroup IV elements on cation exchange resins was developed using molybdenum and tungsten, zirconium and hafnium, respectively, as model elements [1]. Predictions of the sorption properties of elements in ultra trace amounts are difficult because the tracers may behave very different than macroscopic amounts under identical conditions. Speciation calculations using literature data for zirconium hydrolysis [11] and fluoride complexation [12] showed that ZrF_2^{2+} and ZrF_3^+ are the main species in 0.05–0.1 M HCl/ 10^{-4} – 10^{-3} M HF solution [13]. According to this speciation, the subgroup IV elements zirconium and hafnium should sorb on cation exchange resins, which we could recently confirm experimentally [1].

Literature data on complex stability constants of mononuclear complexes for subgroup VI elements are very sparse, so that no preliminary calculations can be done to determine the species for the conditions of interest. For uranium, however, the stability constants for the complexation with fluoride and chloride are well known [14]. Fig. 1 shows the calculated composition of uranium species as a function of the HF concentration at several constant HCl concentrations. The following formation constants were used: $\lg K_1 = 4.54$, $\lg K_2 = 3.34$, $\lg K_3 = 2.57$ and $\lg K_4 = 1.34$ that are given by the NEA Thermodynamic Data Bank [14]. The cations UO_2^{2+} and UO_2F^+ are the main species between 10^{-1} – 10^{-3} M HF, and, therefore, should be

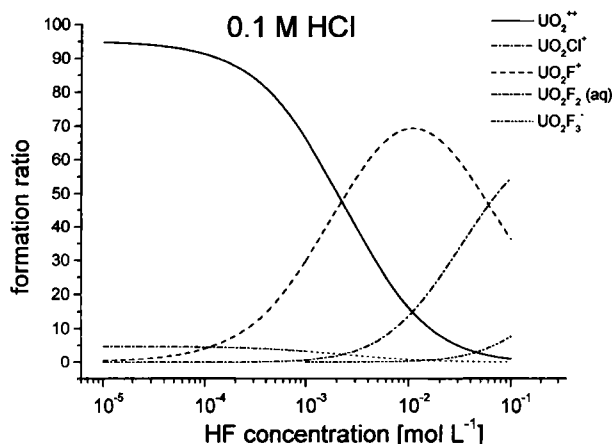


Fig. 1. Formation ratios of U(VI) fluoride species as a function of HF concentration, $[\text{H}^+] = 0.1$ M, no consideration of mixed-ligand compounds.

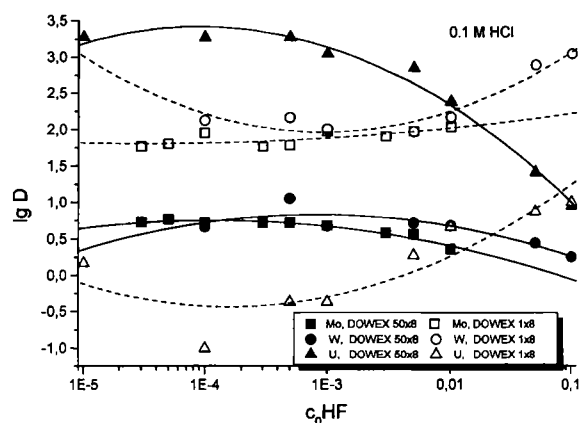


Fig. 2. Distribution coefficients of U, W and Mo on DOWEX 50X8 and DOWEX 1X8 as a function of the HF concentration at 0.1 M HCl.

adsorbed on cation exchangers. The calculations show that chloride complexation plays only a minor role in this concentration range, and was therefore not considered.

Adsorption of uranium, tungsten and molybdenum on anion exchange resins from mixed HCl/HF solutions was studied by Kraus *et al.* [15, 16]. They found a minimum adsorption for uranium at a HCl concentration of 0.1 M at a constant HF concentration of 1.0 M. Only slight sorption of uranium was found with 0.1 M HCl/0.1 M HF [17]. This means that in this concentration range the formation of positively charged fluoride-containing complexes takes place, which are destroyed if the fluoride or chloride concentration increases and neutral and anionic complexes are formed. For molybdenum and tungsten, such a minimum in the adsorption behaviour exists only at high HCl concentrations (2–8 M, [16]). Very diluted HF concentrations ($<10^{-3}$ M) have not been studied at all.

The experimentally determined sorption behaviour of uranium under the selected conditions can be seen in Fig. 2. The sorption of ^{232}U on DOWEX 50X8 and

DOWEX 1X8 is shown as a function of the HF concentration at constant HCl concentrations of 0.1 M. To compare this behaviour with that of tungsten and molybdenum, their sorption behaviour is also depicted in this figure. These sorption studies were carried out earlier under the same conditions as the uranium study; the details of sample preparation and performance were given earlier [1]. Uranium is sorbed onto the cation exchanger over a wide range of HF concentrations. Only at HF concentrations higher than 0.01 M, desorption of uranium from the cation exchange resin takes place. This behaviour confirms our calculations. On the anion exchanger, there is no sorption up to HF concentrations of 0.01 M, then slight sorption begins. These results confirm the values of Faris *et al.* [17] and also expand the knowledge about the chemical properties at concentration ranges between 10^{-5} and 0.1 M HF.

The sorption behaviour of molybdenum and tungsten completely differs from that of uranium on both the cation and the anion exchange resins. This is probably due to the different electronic structure of the uranyl ion in comparison with molybdenum and tungsten compounds. Available f-orbitals lead to a linear geometry of the O-U-O group. Due to participation of π -bonding the bonding length is very short. The consequence is very strong bonding of the oxygen atoms and high stability of the UO_2^{2+} -group [18]. Such a structure cannot be explained with pure d-orbital bonding and is not known for tungsten and molybdenum. The absence of a dipole moment and the more basic character of the uranyl ion due to its larger ionic radius, in comparison to tungsten and molybdenum, result in a low tendency to hydrolyze. Because of this, for instance, anions of the form MO_4^{2-} are not known for uranium. This higher stability of cationic uranium species is the reason for its stronger sorption on cation exchangers in comparison to tungsten and molybdenum.

To further study the chemical properties of trace amounts of uranium in this system, we determined $\lg D$ values on DOWEX 50X8 and on DOWEX 1X8 in dependence on the HCl concentration at constant HF concentrations of 10^{-4} M and 10^{-3} M, respectively (Fig. 3). Desorption of uranium from the cation exchanger takes only place at HCl concentrations above 0.5 M. Simultaneously the sorption onto the anion exchanger increases, which is due to the formation of negatively charged chloride complexes at high HCl concentrations. This also agrees very well with literature data [16]. We reported the behaviour of tungsten and molybdenum under these conditions earlier [1]. Their adsorption on both the cation and the anion exchanger differs completely from that of uranium over a wide range of HCl concentrations.

Pershina *et al.* [19] predicted on the basis of DS DVM calculations analog behaviour between seaborgium and molybdenum and tungsten, and no similarities with uranium. Our experimental results on the sorption behaviour of uranium in diluted HCl/HF sys-

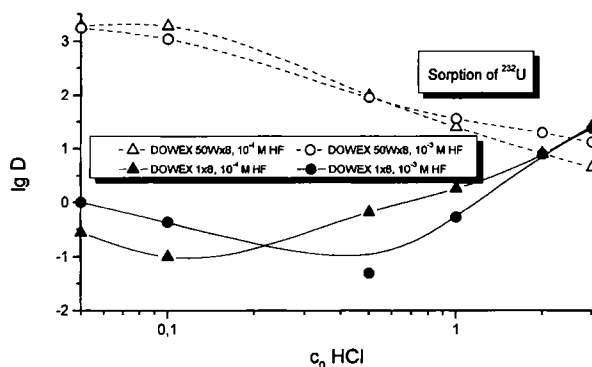


Fig. 3. Distribution coefficients of U on DOWEX 50X8 and DOWEX 1X8 as a function of the HCl concentration at 1.0×10^{-4} M HF and 1.0×10^{-3} M HF.

tems confirm this assumption. From the results on the sorption behaviour of seaborgium in 0.1 M HNO_3 / 5×10^{-4} M HF [4] follows that it is a typical member of subgroup VI and does not behave like the pseudohomolog uranium.

Summary

Batch studies with ^{232}U showed that in the concentration intervals 10^{-4} – 10^{-2} M HF and 10^{-2} –1.0 M HCl uranium is completely adsorbed onto the strongly acid cation exchanger DOWEX 50X8 in contrast to molybdenum and tungsten that show completely different sorption properties under these conditions [1]. Since seaborgium could be successfully separated from a similar solution [4], we concluded that it behaves like its lighter homologs tungsten and molybdenum and not like the pseudohomolog uranium. Therefore, the system is not only well-suited for the separation and identification of seaborgium but also for the determination of its chemical properties. Under some conditions even tungsten and molybdenum show slight different sorption properties on DOWEX 50X8 in these solutions [1]. This should open the possibility to distinguish also between a tungsten or molybdenum like behaviour of seaborgium, if conditions could be found under which the sorption of these two elements completely differs from each other.

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