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Journal of Alloys and Compounds 271–273 (1998) 292–295

Journal of ALLOYS AND COMPOUNDS

# Extraction of the fluoride-, chloride- and bromide complexes of the elements Nb, Ta, Pa, and 105 into aliphatic amines

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## Abstract

Previous studies of the halide complex formation of element 105 in HCl–HF mixtures and extractions into triisooctyl amine (TIOA) have been performed with the Automated Rapid Chemistry Apparatus, ARCA II. Element 105 was shown to be absorbed on the column from 12 M HCl–0.02 M HF together with its lighter homologues Nb, Ta and the pseudohomologue Pa. In elutions with 10 M HCl–0.025 M HF, 4 M HCl–0.02 M HF, and 0.5 M HCl–0.01 M HF, the extraction sequence Ta>Nb>105>Pa was observed and element 105 behaved very differently from its closest homologue Ta. As it is not possible within reasonable effort to model the many presumably mixed fluoride–chloride complexes involved in these studies, theoretical calculations were performed in the pure chloride system predicting a reversed sequence of extraction. To verify this experimentally, and in order to perform a systematic study of halide complexation of the group 5 elements, new batch extraction experiments for Nb, Ta, and Pa were performed with the quarternary ammonium salt Aliquat 336 in pure HF, HCl, and HBr solutions. Based on these results, new chromatographic column separations were elaborated to study separately the fluoride and chloride complexation of element 105 with ARCA II. In the system Aliquat 336–HF, after feeding of the activity onto the column in 0.5 M HF, element 105 did not elute in 4 M HF (Pa fraction) but showed a higher distribution coefficient close to that of Nb (and Ta). In the system Aliquat 336–HCl, after feeding onto the column in 10 M HCl, element 105 showed a distribution coefficient in 6 M HCl close to that of Nb establishing an extraction sequence Pa>Nb≥105>Ta which is theoretically predicted by considering the competition between hydrolysis and complex formation. © 1998 Elsevier Science S.A.

*Keywords:* Niobium; Tantalum; Protactinium and element 105; Extraction chromatography; Aliquat 336–HCl; Aliquat 336–HF

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## 1. Introduction

Previous studies of the aqueous chemistry of element 105 have provided expected results as well as surprises. These results are reviewed in [1]. In one of these experiments, anion exchange chromatographic separations using triisooctyl amine (TIOA) on an inert support were performed with the Automated Rapid Chemistry Apparatus (ARCA II) [2] and were used to investigate the halide complexation of element 105 relative to that of its lighter homologues and the pseudohomologue Pa [3,4]. Element 105 was shown to extract into TIOA from 12 M HCl–0.02 M HF analogous to Nb, Ta, and Pa by forming either negative or polynegative anions. In elutions with 10 M HCl–0.025 M HF, 4 M HCl–0.02 M HF, and 0.5 M HCl–0.01 M HF, the extraction sequence Ta>Nb>105>Pa was observed and element 105 behaved very differently from its closest homologue Ta. The nonTantalum-like behaviour is corroborated by theoretical calculations [5] in which element 105 was found to preferentially form oxyhalide complexes, presumably $MOX_4^-$ (X=Cl,F), which are also predominant for Nb and Pa. For Ta, pure halide complexes such as $TaX_6^-$ are predominant over a wide range of halide concentrations.

To predict the extractability of the oxygen containing chloride complexes of Nb, Pa, and Element 105, Born's theory for the transfer of ions from the aqueous phase into the organic phase was applied [5] with the result that Pa should always show higher partition coefficients than Nb and, due to the size of the complex ions, element 105 should show an intermediate behaviour. This is the opposite sequence as compared to the experimental one. The apparent discrepancy was tentatively attributed [5] to the

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PII: S0925-8388(98)00073-5

presence of fluoride ions in the experiments [3,4] which might result in the formation of multiply charged fluoride or mixed fluoride–chloride complexes showing a different extraction behaviour. Thus, new experiments in which the group-5 elements are extracted from pure HCl solutions were strongly suggested [5].

Therefore, in the present work, a systematic study of the extraction of the group-5 elements from pure HF, HCl, and HBr solutions into aliphatic amines was performed. Based on these results, chromatographic separations of the group-5 elements and element 105 with ARCA II were carried out in the HF and HCl system. From the respective elution positions of element 105, its distribution coefficients are determined and compared to new theoretical predictions [6] in which the competition between hydrolysis and halide complex formation is explicitly taken into account.

## 2. Experimental

### 2.1. Chemicals and tracer solutions

The aliphatic amines triisooctl amine (TIOA), tri-*n*-octyl amine (TOA), tricaprylyl amine (Alamine 336), and methyl-tricaprylyl ammonium chloride (Aliquat 336) were purchased from Merck, Fluka, and General Mills, respectively, and were used as received. Sieved Voltalef powder from Lehmann and Voss, Hamburg, was used to sorb the amines with a particle size of 125–250 μm for the batch extractions and 30–80 μm for the chromatographic column experiments. Different weight ratios of amine to support in the range of 1:3 to 1:8 were used. The Voltalef powder was mixed with a solution of the amines in cyclohexane, which was subsequently evaporated by stirring at room temperature.

The tracers used in the batch experiments and column separations were $^{95}$Zr, $^{175}$Hf, $^{95}$Nb, $^{177,179}$Ta, and $^{233}$Pa. $^{95}$Zr and $^{95}$Nb were purchased from CIS Diagnostik, Dreieich, or were separated from $^{235}$U fission products. $^{233}$Pa was obtained as the $\beta^-$-decay product of $^{233}$Th from neutron-irradiated Th. All neutron irradiations were performed at the TRIGA-reactor, Mainz. $^{177}$Ta was produced in a 40 MeV α-particle bombardment of a Lutetiumoxide-Target and $^{179}$Ta in a 20 MeV proton bombardment of a stack of thin Hf-Targets on 1.5-μm Al backings. In both reactions, $^{175}$Hf was also obtained as a decay product of $^{175}$Ta. These irradiations were performed at the Philips Cyclotron at the Forschungszentrum Karlsruhe.

### 2.2. Extraction- and manually performed column separation experiments

Batches of 0.5 g of the amine–Voltalef powder and 2 ml of acid solution containing the tracer elements were shaken in polyethylene flasks for 2 min. After centrifuging, 1 ml of the aqueous phase and the rest containing 1 ml of the aqueous phase and the organic phase were assayed by γ-spectroscopy. $K_D$ values were calculated from the ratio of the organic phase activity, obtained by subtracting the aqueous phase activity, over the aqueous phase activity by taking into account the volumes of the organic and aqueous phase.

Reversed-phase extraction chromatography separations were manually performed using 1.6×8-mm columns filled with amine–Voltalef (1:5). The flow-rate of the aqueous phase delivered by a HPLC-pump was 1 ml/min. After feeding the tracer activities onto the column from a sample loop, the elements were subsequently eluted by changing the solutions. The fractionally collected samples were assayed for their γ-ray activities.

### 2.3. Production, transport and detection of element 105

The nuclides $^{262,\,263}$105 were produced at the Lawrence Berkeley National Laboratory 88-Inch Cyclotron in the $^{249}$Bk($^{18}$O,5*n*) and the $^{249}$Bk($^{18}$O,4*n*) reactions. A 119.5 MeV $^{18}$O$^{5+}$ beam was passed through a 2.58-mg/cm$^2$ Be window, 0.3 mg/cm$^2$ of $N_2$ cooling gas, and the 2.97 mg/cm$^2$ Be backing to reach the Bk-target material with a projectile energy of 99–100 MeV in the target. The target consisted of 685 μg/cm$^2$ of freshly purified $^{249}$Bk(NO$_3$)$_3$ deposited by molecular plating and converted to the oxide by heating. The production cross sections for the 5*n* and 4*n* reaction channels at a bombarding energy of 99 MeV are 6±3 nb and 2±1 nb [7], respectively. The reaction products recoiling out of the target were stopped in He gas containing KCl or KF aerosols, which were generated by sublimation from a KCl or KF surface at 640°C or 750°C, respectively. The aerosols transported the activities through a 1.57-mm I.D. polyethylene capillary to the collection site in ARCA II where they were deposited by impaction.

Element 105 was detected by α-particles and spontaneous fission (SF) using passivated implanted planar silicon (PIPS) detectors. List mode data were stored for each event including the time after the start of measurement and the detector number in which the event occurred. The detection efficiency for α-particles was 30% and for SF 60%.

## 3. Results

### 3.1. Extraction experiments and manually performed chromatographic separations

The extraction behaviour from pure HCl-solutions of the group 5 elements and Pa was nearly identical for all tested amines. For example, Fig. 1 shows the $K_D$ values of Pa, Nb, Ta, Zr, and Hf for the chloride salt of Aliquat 336 versus HCl concentration. No extraction is observed at

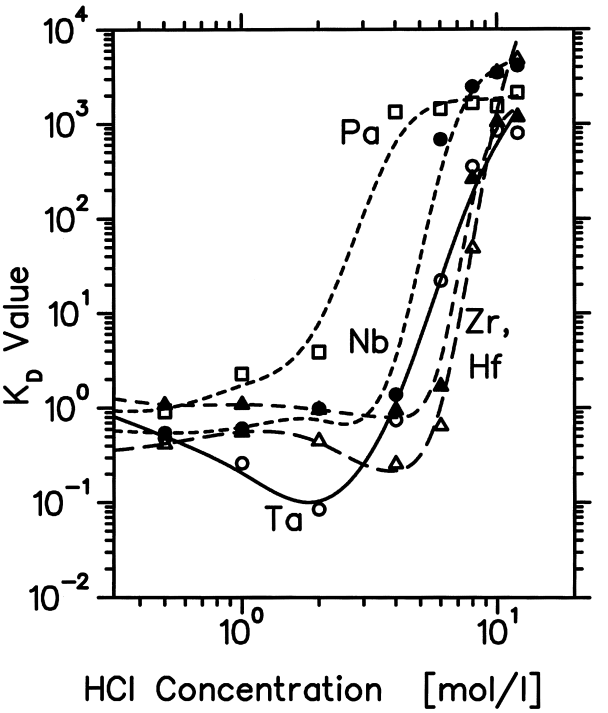

Fig. 1. Extraction behaviour of the elements Pa(□), Nb(●), Ta(○), Zr(▲), and Hf(△) from pure HCl solutions into Aliquat 336. The system shows the inverse extraction sequence Pa>Nb>Ta as compared to the HCl–HF system.

HCl concentrations below 1 M. The sequence of extraction from 1 M to 12 M HCl is Pa>Nb>Ta>Zr,Hf, which is the complete inversion of the known sequence Ta>Nb>Pa in the TIOA–HCl system containing ~0.03 M HF.

In the column experiments, most amines showed a slow kinetics of back extraction into the aqueous phase resulting in elution peaks with an unacceptable tailing of the activities into the subsequent fraction, a feature that is absent in the mixed HCl–HF system [3]. Only with the quarternary amine Aliquat 336, an acceptable chromatographic separation could be achieved. Eu, Nb, Ta, Pa, Zr, and Hf were fed onto the column from 10 M HCl. Zr, Hf, and Ta were eluted in 6 M HCl, Nb in 4 M HCl, and Pa in 0.5 M HCl. Thus, this system allows one to extract the elements from one HCl solution and to differentiate Ta, Nb, and Pa in subsequent elution fractions.

Similarly, new partition experiments and chromatographic separations were performed with the fluoride salt of Aliquat 366–HF and the bromide salt of Aliquat 336–HBr. The $K_D$-values in the HBr system show the same sequence Pa>Nb>Ta as in the HCl system, however, the threshold HBr concentrations from where an appreciable extraction is observed are shifted to higher molarities, i.e. to 6 M for Pa, 9 M for Nb, while Ta is not extracted even for 12 M HBr. Chromatographic separations of Nb and Pa were performed after loading of the activities onto the column in 12 M HBr, by eluting Nb in 7 M HBr and Pa in 2 M HBr.

With the fluoride salt of Aliquat 336, $K_D$-values in the order of $\geq 10^3$ are observed for all elements (Pa>Nb>Ta) already at low HF concentrations in the aqueous phase. These stay high for Nb and Ta up to 12 M HF while they decrease for Pa, Zr, and Hf for >1 M HF. In chromatographic separations, after feeding of the activities onto the column in 0.5 M HF, a Pa fraction was eluted in 4 M HF and Nb and Ta were stripped from the column with 6 M $HNO_3$–0.015 M HF.

### *3.2. Element 105 experiments*

1307 experiments were conducted with element 105 in ARCA II, 930 for the Aliquat 336–HCl system with a 50-s cyclic collection time of the aerosol. Because of the high mineral acid concentrations, a Kel-F slider was used to collect the activities in ARCA II. The reaction products were fed onto the columns in 167 μl of 10 M HCl followed by an elution of 183 μl of 6 M HCl (Ta fraction) and 167 μl of 6 M $HNO_3$–0.015 M HF (Nb, Pa fraction). The samples were evaporated to dryness on Ta disks. An energy window from 8.25 to 8.68 MeV was selected to search for the $\alpha$-decays of the 34-s $^{262}$105 (8.45, 8.53, 8.67 MeV), 27-s $^{263}$105 (8.36 MeV) and their daughters, 3.9-s $^{258}$Lr (8.57-8.65 MeV) and 5.4-s $^{259}$Lr (8.45 MeV), including time correlated pairs of mother–daughter decays of these nuclides. The counting time for each sample was 7 min.

Three pairs of correlated mother–daughter decays were registered in the Aliquat 336–HCl system. They are observed both in the Ta-fraction (1) and in the Nb, Pa fraction (2).

The random correlation rate was determined by a Monte-Carlo simulation considering the total number of $\alpha$-events in each fraction. For the Ta fraction, the number of random correlations was 0.108 for a correlation time below 20 s so that the probability for the correlation to be random is 9.7%. In the Nb, Pa fraction the predicted number of random correlation was 0.093 and the probability for them to be random was 0.4%. From this we conclude that the three observed correlations are likely to be true correlations.

If single $\alpha$-events in the chemical fractions are considered, the events from $^{211m}$Po and $^{212\text{-}m3}$Po contamination and the background from cosmic rays, electronic noise, etc. has to be substracted. Based on the resulting numbers of $\alpha$-events in each fraction and the volumes of both phases, we calculate a $K_D$ value for element 105 in 6 M HCl of $508^{+692}_{-237}$, which is close to that of Nb and differs from the values for Pa and Ta, see Fig. 1.

In the Aliquat 336–HF system, 377 experiments with ARCA II were performed. The dissolved reaction products were loaded on the column with 167 μl of 0.5 M HF. In elutions with 133 μl of 4 M HF (Pa fraction), and with 167 μl of 6 M $HNO_3$–0.015 M HF (Nb, Ta fraction) 4 time-correlated $\alpha\alpha$-decays were detected in the 8.25 to

8.68 MeV energy window. All correlations were observed in the Nb, Ta fraction and none in the Pa fraction. The number of random correlations in the Nb, Pa fractions has been calculated to be 0.737 and the probability for all observed correlations to be random is 0.6%.

Because in the HF experiments, the Po contamination was larger than in the HCl experiments, the number of single $\alpha$-events was not considered for determining the $K_D$ value.

Therefore, we have calculated the $K_D$ value from the ratio of the probability distributions for none and four observed correlated events. This results in a lower limit for the $K_D$ value of element 105 in 4 M HF of $>570$, which is close to that of Nb and Ta ($\geq 10^3$) and differs from Pa (~10).

## 4. Discussion

Our new investigations by reversed-phase anion exchange chromatography with Aliquat 336 of the pure chloride complexation of element 105 in comparison with its homologues Nb and Ta, and to the pseudohomologue Pa have shown a new extraction sequence Pa>Nb≥105>Ta. This is an inversion of the earlier observed [3,4] sequence with TIOA in the mixed HCl–HF system Ta>Nb>105>Pa. Apparently, the extraction behaviour of some elements (presumably Pa and Ta) in the mixed HCl–HF system cannot be explained by pure chloride complexation but by the formation of mixed chlorofluoro ions or even pure fluoro complexes (for Ta). In the clearer case of the pure halide acid solutions, the results for amine extractions from pure HF, HCl, and HBr solutions are in agreement with theoretical considerations of the competition between hydrolysis and complex formation/extraction:

$$M(OH)_6^- + 4HX \overset{\Delta E}{\leftrightarrows} MOX_4^- + 5H_2O \qquad (1)$$

V. Pershina [6] has made estimates of the free energy change of the complex formation in Eq. (1) using results of calculations of the electronic structure of $M(OH)_6^-$ and $MOX_4^-$ for Nb, Ta, Ha and Pa with an improved Dirac–Slater DV code. Due to predominant changes in the electrostatic part of the interaction energy, the total energy differences $\Delta E$ have been shown to decrease in the order Ta>105>Nb>Pa. This means that hydrolysis is the strongest for Ta and the least for Pa.

In combination with Eq. (1), this means that it takes the highest HCl concentration to get the Ta complexed and extracted and Pa being extracted at the lowest threshold HCl concentration in agreement with Fig. 1. The predicted [6] sequence of extraction is thus Pa>Nb≥105>Ta.

Interestingly, the values of $\Delta E$ calculated in [6] are in the order of 12 eV for the fluorides, 20 eV for the chlorides and 22 eV for the bromides (not taking into account the enthalpy of formation of $H_2O$ which is 3 eV). This is nicely in agreement with the experimental findings: For the fluorides, the equilibrium is always on the right hand side of Eq. (1) even at low HF concentrations; for the chlorides it takes >3 M HCl to form extractable chloride complexes and for the bromides the threshold is shifted to >6 M HBr.

It is concluded that the amine extraction behaviour of element 105 halide complexes is always close to that of its lighter homologue Nb. In pure HF solutions, it differs mostly from the behaviour of Pa. In pure HCl solutions, it differs considerably from both Pa and Ta. In mixed HCl–HF solutions, it differs markedly from the behaviour of Ta.

## Acknowledgements

The authors are indepted to the Division of Chemical Sciences of the Office of Basic Energy Science of the U.S. Department of Energy for making the $^{249}$Bk-target material available through the transplutonium element production facilities at the Oak Ridge National Laboratory. We wish to thank the staff and crew of the LBL 88-Inch Cyclotron for their assistance in providing the $^{18}$O beams. This work was supported in part by the Deutsche Forschungsgemeinschaft under contract numbers Kr 1458/2-1 and Kr 1458/2-2.

## References

[1] J.V. Kratz, Proceedings of the International Conference on Actinides, Santa Fe, New Mexico, USA, September 19–24, 1993, J. Alloys Comp. 213/214, (1994) 20.
[2] M. Schädel, W. Brüchle, E. Jäger, E. Schimpf, J.V. Kratz, U.W. Scherer, H.P. Zimmermann, Radiochim. Acta 48 (1989) 171.
[3] J.V. Kratz, H.P. Zimmermann, U.W. Scherer, M. Schädel, W. Brüchle, K.E. Gregorich, R.A. Henderson, D.M. Lee, M.J. Nurmia, H.L. Hall, C.M. Gannett, J.D. Leyba, D.C. Hoffman, H. Gäggeler, D. Jost, J. Kovacs, U.W. Scherer, A. Weber, Radiochim. Acta 48 (1989) 121.
[4] H.P. Zimmermann, M.K. Gober, J.V. Kratz, M. Schädel, W. Brüchle, E. Schimpf, K.E. Gregorich, A. Türler, K.R. Czerwinski, N.J. Hannink, B. Kadkhodayan, D.M. Lee, M.J. Nurmia, D.C. Hoffman, H. Gäggeler, D. Jost, J. Kovacs, U.W. Scherer, A. Weber, Radiochim. Acta 60 (1993) 11.
[5] V. Pershina, B. Fricke, J.V. Kratz, G.V. Ionova, Radiochim. Acta 64 (1994) 37.
[6] V. Pershina, Radiochim. Acta, in press.
[7] J.V. Kratz, H.P. Zimmermann, M.K. Gober, M. Schädel, W. Brüchle, E. Schimpf, K.E. Gregorich, A. Türler, K.R. Czerwinski, N.J. Hannink, B. Kadkhodayan, D.M. Lee, M.J. Nurmia, D.C. Hoffman, H. Gäggeler, D. Jost, J. Kovacs, U.W. Scherer, A. Weber, Phys. Rev. C 45 (1992) 1064.