SOLVENT EXTRACTION OF HAFNIUM(IV)

XXII. EXTRACTION BY N-BENZOYL-N-PHENYL HYDROXYLAMINE FROM WATER—DIMETHYL SULFOXIDE AND WATER—DIMETHYL FORMAMIDE SOLUTIONS*

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Solvent extraction of $^{175,181}$Hf(IV) into solutions of HBPHA** in CHCl₃, tetrachloroethane (C₂H₂Cl₄), CCl₄ and benzene from mixtures of water with DMSO or DMFA at 2M HClO₄ formal acidity was studied. With diluents containing acidic hydrogen (CHCl₃, C₂H₂Cl₄) the presence of DMSO or DMFA in the extraction system leads to an increased extractability of the Hf(IV) chelate. Possible reasons for this synergism are discussed. Extractions into benzene and CCl₄, as well as those into CHCl₃ and C₂H₂Cl₄ at high DMSO and DMFA concentrations, are antagonistic. This is caused by the decrease of the partition coefficient of HBPHA, and changes in the solvation of Hf(IV) ion in the polar phase. The latter effect is very strong at high DMSO concentrations, and with macroconcentrations of Hf(IV) finally leads to precipitation of crystalline adducts Hf(ClO₄)₄ · xDMSO (x = 7 – 8).

Introduction

It has been shown by ALLAN et al.¹⁻³ that the changes in metal partition occurring when a polar organic solvent miscible with water is introduced into a common two phase extraction system can be advantageous for radiochemical separations. We have recently studied systems involving Hf(IV) and chelating extractants⁴,⁵ where synergism and antagonism were produced by using aqueous-alcoholic solutions. During subsequent systematic search for other possible synergistic systems of this kind we have found that DMSO and DMFA in combination with HBPHA as the extracting agent showed interesting behaviour with respect to the extraction of hafnium(IV). The results of this study are reported in this paper.

**Abbreviations used throughout the text: HBPHA, DMSO, and DMFA for N-benzyol-N-phenyl hydroxylamine, dimethyl sulfoxide, and dimethyl formamide, respectively.

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Experimental

Radioactive tracers

The $^{175,181}$Hf tracer was supplied as HfO$_2$ (USSR) with an initial specific activity of 1570 mCi/g. The preparation of the stock solution of $^{175,181}$Hf(IV) in 10M HClO$_4$ was described elsewhere. $^{6}$ $^{35}$S-labelled DMSO, specific activity 1.7 mCi/mmol, was obtained from The Radiochemical Centre, Amersham, England.

Chemicals

N-benzoyl-N-phenyl hydroxylamine (Lachema, Czechoslovakia) was used as the extraction agent for Hf(IV). C$_2$H$_2$Cl$_4$ and CCl$_4$ were purified from polar impurities on a column of Brockmann alumina, and distilled before use. DMSO (Fluka) was cooled below m.p., the liquid fraction was discarded, the crystalline solid was allowed to melt and distilled under vacuum at 85 $^\circ$C. DMFA (Loba-Chemie, Austria) was distilled under vacuum at 65 $^\circ$C. Benzene, CHCl$_3$, and other chemicals were of reagent grade quality.

Procedures

The extraction of hafnium and the partition of HBPHA were carried out in the same way as described earlier. $^{4}$ Distribution ratio of hafnium, D, was expressed as the ratio of organic to aqueous $\gamma$-activities, and corrected for volume changes. $^{4}$ Activity was measured in 2 ml aliquots after extraction in a 3"Nal(Tl) well-type scintillation crystal of the 1185 automatic gamma counting system of Nuclear Chicago.

Partition of DMSO was studied with DMSO-$^{35}$S in the same way as described for labelled alcohols. $^{4}$ In each experiment approximately 5 $\mu$Ci $^{35}$S-DMSO was used.

UV spectra of HBPHA were recorded in 1 cm quartz cuvettes by using a Spectromom 201 MOM spectrophotometer (Hungary).

Solid adducts of Hf(ClO$_4$)$_4$ with DMSO were prepared by shaking or by keeping a 0.012M Hf(IV) solution in 1.8M HClO$_4$ containing DMSO overnight. The solid was filtered, washed with a small amount of acetone, and dried over P$_2$O$_5$. The adducts were analyzed for Hf(IV) by complexometric titration using xylenol orange as indicator, $^{7}$ and for C and H by elemental analysis using Carlo Erba Elemental Analyzer 1102 (Italy).