EXTRACTION OF HAFNIUM(IV)
WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE SOLUTIONS
FROM STRONGLY ACID SOLUTIONS CONTAINING DIMETHYL
SULPHOXIDE OR HEXAMETHYLPHOSPHOR TRIAMIDE

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The extraction of hafnium(IV) with N-benzoyl-N-phenylhydroxylamine solutions in chloroform or toluene from strongly acid ($HClO_4$) solutions of dimethyl sulfoxide or hexamethylphosphor triamide has been studied. These substances were found to suppress the conversion of the extraction mechanism from ion exchange to solvation: while in solutions free of these substances this conversion takes place at $HClO_4$ concentrations of about 4 mol l^{-1}, in the mixed aqueous–organic (polar) phase the requisite acid concentrations are considerably higher. The possible causes of this effect are discussed.

This work is a part of our systematic study of the synergistic and antagonistic effects occurring during the extraction of hafnium(IV) with chelating agents from mixed aqueous-organic media[1−4]. Previously[4] we have been concerned with the extraction of Hf(IV) with N-benzoyl N-phenylhydroxylamine (HBPHA) from 2M-$HClO_4$ in the presence of hexamethylphosphor triamide (HMPT) or trimethylphosphate (TMP), where these substances were found to promote the extraction of hafnium complexes into solvents containing acid hydrogen (chloroform, tetrachloroethane) while in case of tetrachloromethane or benzene antagonism only occurs. Similar results obtained for the extraction of hafnium from dimethyl sulphoxide (DMSO) or dimethylformamide (DMF) have been discussed[3] in terms of the formation of a hafnium complex in which the basic molecule is bonded directly to the hafnium atom by a coordination bond, or of an increased solubility (or solvation) of the hafnium chelate in the chloroform phase, which contains a large quantity of the basic solvent due to its high distribution. The present work is a direct continuation of our previous investigation[4] of the extraction of hafnium from 2M-$HClO_4$ in the presence of TMP or HMPT.

EXPERIMENTAL

The organic phase was formed by a solution of N-benzoyl-N-phenylhydroxylamine in chloroform or toluene of reagent grade purity (all Lachema, Czechoslovakia). The mixed aqueous–orga-

nic phase ("polar phase") was combined from aqueous $HClO_4$ of reagent grade purity (Lachema, Czechoslovakia) and dimethyl sulphoxide or hexamethylphosphor triamide of the same purity (Fluka, Switzerland), and a $^{175+181}Hf$ radioactive tracer (Radiochemical Centre, Swierk, Poland) was added. The volumes of both phases were 5 cm³. The preparation of the stock solution of hafnium and the extraction procedure were as described previously[1-3].

After the extraction, 2 cm³ aliquots were taken and their activity was measured on a Nuclear Chicago 1185 automatic gamma counting system fitted with a well-type NaI(Tl) scintillation crystal. The hafnium distribution ratio (D) was calculated as the ratio of the organic to polar phase activities; corrections for volume changes were made where necessary.

RESULTS AND DISCUSSION

The effect of the concentration of DMSO in the polar phase on the distribution of hafnium extracted with 10^{-3}M-HBPHA in chloroform is shown in Fig. 1 for various acidities of the polar phase. For the extraction from 2M and 4M-HClO$_4$, the distribution ratio increases with increasing concentration of DMSO up to a maximum at $c_{DMSO} \approx 0.6$ mol l^{-1}; a steady decrease follows at higher DMSO concentrations. For the extraction from 6M or 8M-HClO$_4$, the distribution ratio is nearly constant starting from low DMSO concentrations or it decreases slightly; at DMSO concentrations above 0.3 mol l^{-1} the decrease becomes more pronounced.
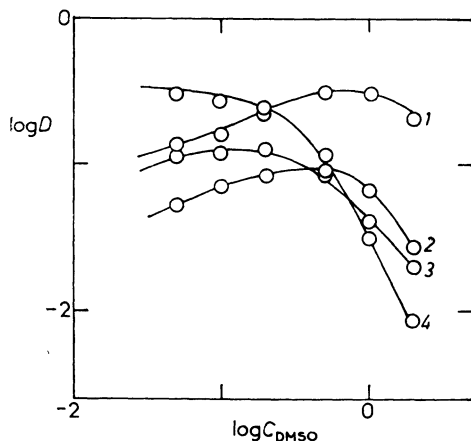

FIG. 1

Dependence of the hafnium distribution ratio on the concentration of DMSO. $c_{Hf} = 2.12$ . . 10^{-7} mol l^{-1}, extractant: $1 . 10^{-3}$M- -HBPHA in chloroform. Concentration of HClO$_4$ in the polar phase (mol l^{-1}): *1* 2, *2* 4, *3* 6, *4* 8
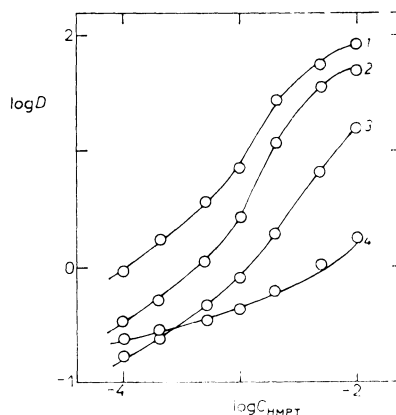

FIG. 2

Dependence of the hafnium distribution ratio on the concentration of HMPT. $c_{Hf} = 2.12 . 10^{-7}$ mol l^{-1}, extractant: 1 . . 10^{-3}M-HBPHA in chloroform. Concentration of HClO$_4$ in the polar phase (mol . . l^{-1}): *1* 2, *2* 4, *3* 6, *4* 8

The situation is entirely different with HMPT used in concentrations from 10^{-4} to $10^{-2}\,\text{mol}\,1^{-1}$ (Fig. 2). The hafnium distribution ratio invariably increases with increasing concentration of HMPT, in the extraction conditions used almost about two orders of magnitude. These results, which are consistent with those obtained previously[4], bear out the concept of forming a hafnium synergic complex with HMPT in which the basic solvent is bonded directly to the metal atom[4].

The dependence of the hafnium distribution ratio on the initial concentration of perchloric acid in the polar phase, for the system with DMSO and chloroform as solvent, is shown in Fig. 3. In the absence of DMSO a minimum appears on the plot at $c_{\text{HClO}_4} \approx 4\,\text{mol}\,1^{-1}$, due to the extraction mechanism converting from ion exchange to solvation[5]. With increasing DMSO concentration in the polar phase up to $\sim 0.5\,\text{mol}\,1^{-1}$, the curves are displaced to higher D values, the minimum is shifted to higher acidities at the same time, and the slope of the tangent to curves in their descending part increases slightly. For the extraction from 1M DMSO,
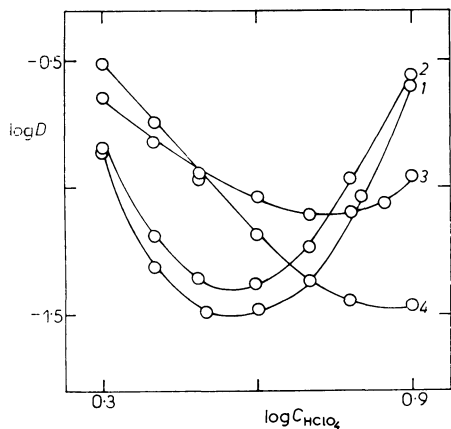

FIG. 3

Effect of the concentration of perchloric acid on the hafnium distribution ratio in the presence of DMSO. $c_{\text{Hf}} = 2\cdot12 \,.\, 10^{-7}\,\text{mol}\,.\,.1^{-1}$, extractant: $1\,.\,10^{-3}$M-HBPHA in chloroform. Concentration of DMSO (mol 1^{-1}): *1* 0, *2* 0·05, *3* 0·5, *4* 1
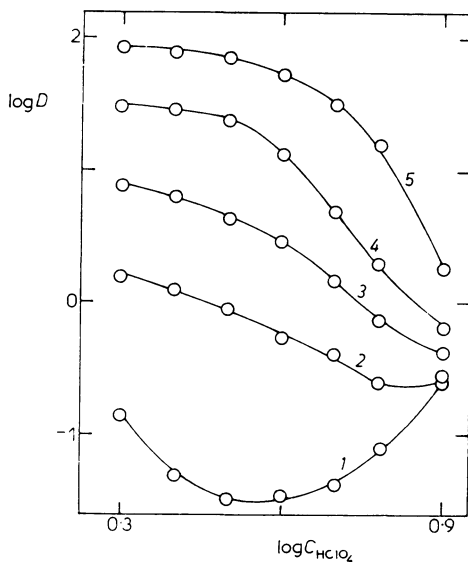
FIG. 4

Effect of the concentration of perchloric acid on the hafnium distribution ratio in the presence of HMPT. $c_{\text{Hf}} = 2\cdot12\,.\,10^{-7}$ mol 1^{-1}, extractant: $1\,.\,10^{-3}$M-HBPHA in chloroform. Concentration of HMPT (mol 1^{-1}): *1* 0, *2* $5\,.\,10^{-4}$, *3* $1\,.\,10^{-3}$, *4* $5\,.\,10^{-3}$, *5* $1\,.\,10^{-2}$

the hafnium distribution decreases monotonically up to $HClO_4$ concentration of about $7 \, mol \, l^{-1}$.

Significant changes in the $\log D$ vs $\log c_{HClO_4}$ plots induced by HMPT appear even if this agent is present in low concentrations (Fig. 4). Its synergistic effect

TABLE I

Slope of the dependence $\log D = f(\log c_{HBPHA})$ in the absence of organic substance and in the presence of dimethyl sulfoxide ($0.5 \, mol \, l^{-1}$) and hexamethylphosphor triamide ($5 \, mmol \, l^{-1}$), respectively

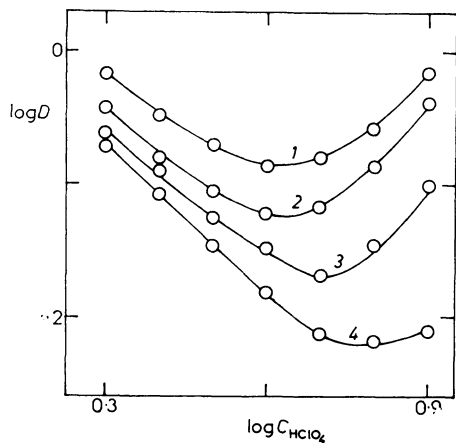| c_{HClO_4} $mol \, l^{-1}$	Slope, in the presence of		
	—	DMSO	HMPT
2·0	2·60	2·10	0·8
3·5	2·35	2·0	0·8
7·0	2·35	2·0	0·7

FIG. 5

Effect of the concentration of perchloric acid on the hafnium distribution ratio in the presence of DMSO, extraction into toluene. $c_{Hf} = 2·12 . 10^{-7} \, mol \, l^{-1}$, $c_{HBPHA} = 1 . 10^{-3} \, mol \, l^{-1}$. Concentration of DMSO ($mol \, l^{-1}$): 1 0, 2 0·05, 3 0·5, 4 1
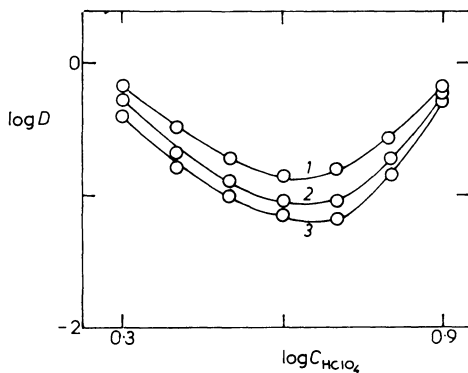
FIG. 6

Effect of the concentration of perchloric acid on the hafnium distribution ratio in the presence of HMPT, extraction into toluene. $c_{Hf} = 2·12 . 10^{-7} \, mol \, l^{-1}$, $c_{HBPHA} = 1 . 10^{-3} \, mol \, l^{-1}$. Concentration of HMPT ($mol \, l^{-1}$): 1 0, 2 5 . 10^{-4}, 3 5 . 10^{-3}

is substantially more marked than that of DMSO, clearly due to the considerably higher basicity of the phosphoryl oxygen. The minimum which indicates the change in the mechanism, vanishes completely and a descending plot is obtained.

For a comparison, the dependences were also examined with toluene as solvent (Figs 5 and 6). The minimum appears here, too, it is only shifted toward higher acidities or lower distribution ratios, due to changes in the distribution of the extracting agent[6].

The results indicate that the effect of acidity is most pronounced in systems where the organic phase solvent contains an acidic hydrogen $(CHCl_3)$.

The slope of the plot $\log D$ vs $\log c_{HBPHA}$ was measured for various acidities and in the absence or presence of the organic substances. As the data of Table I demonstrate, the slope decreases if the substances are present. It has been shown[7] that from 2M-$HClO_4$, hafnium is extracted in the form of $Hf(BPHA)_4$ chelate, stepwise formation of charged complexes in the aqueous phase being conceivable[6]. The decrease in the slope of the dependence in question is probably due to the charged complexes in the polar phase being formed to a greater extent; such a decrease also has been observed previously[1-4]. HMPT is seen to affect the slope substantially more than DMSO. This is also consistent with the shift of the minimum to higher acidities or its complete elimination in the case of HMPT. The formation of charged complexes in the polar phase prevents the change in the extraction mechanism, i.e. the formation of the $Hf(ClO_4)_4$. 4 HBPHA species[5]. With polar aqueous-organic phases, occurrence of low extractable complexes of hafnium with DMSO or HMPT in the polar phase is also conceivable, the formation of the solvated hafnium perchlorate being thereby hindered.

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